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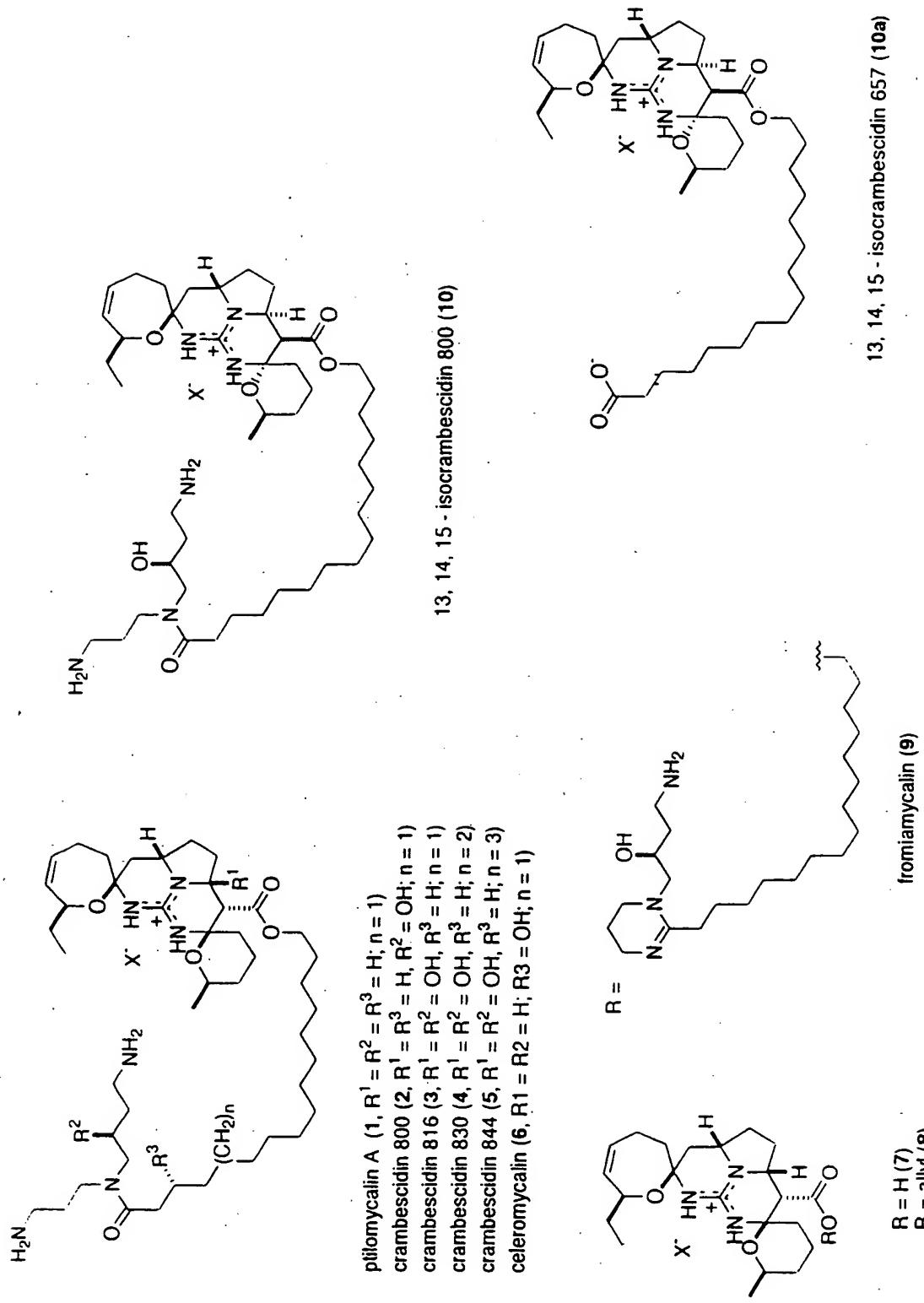


Figure 1

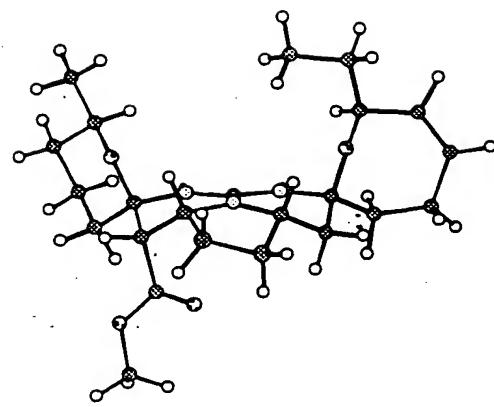


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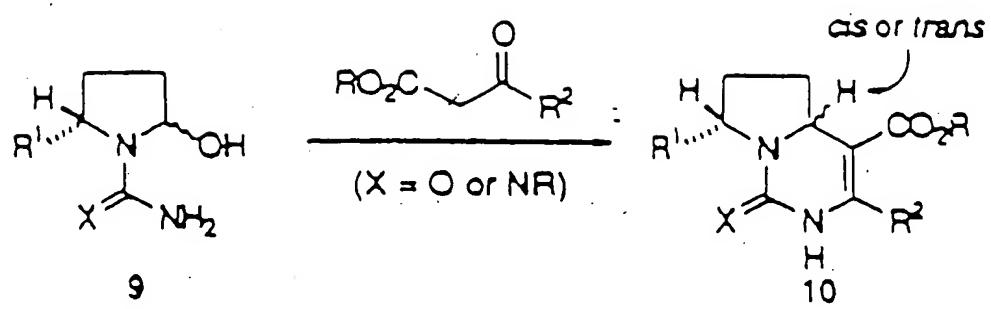
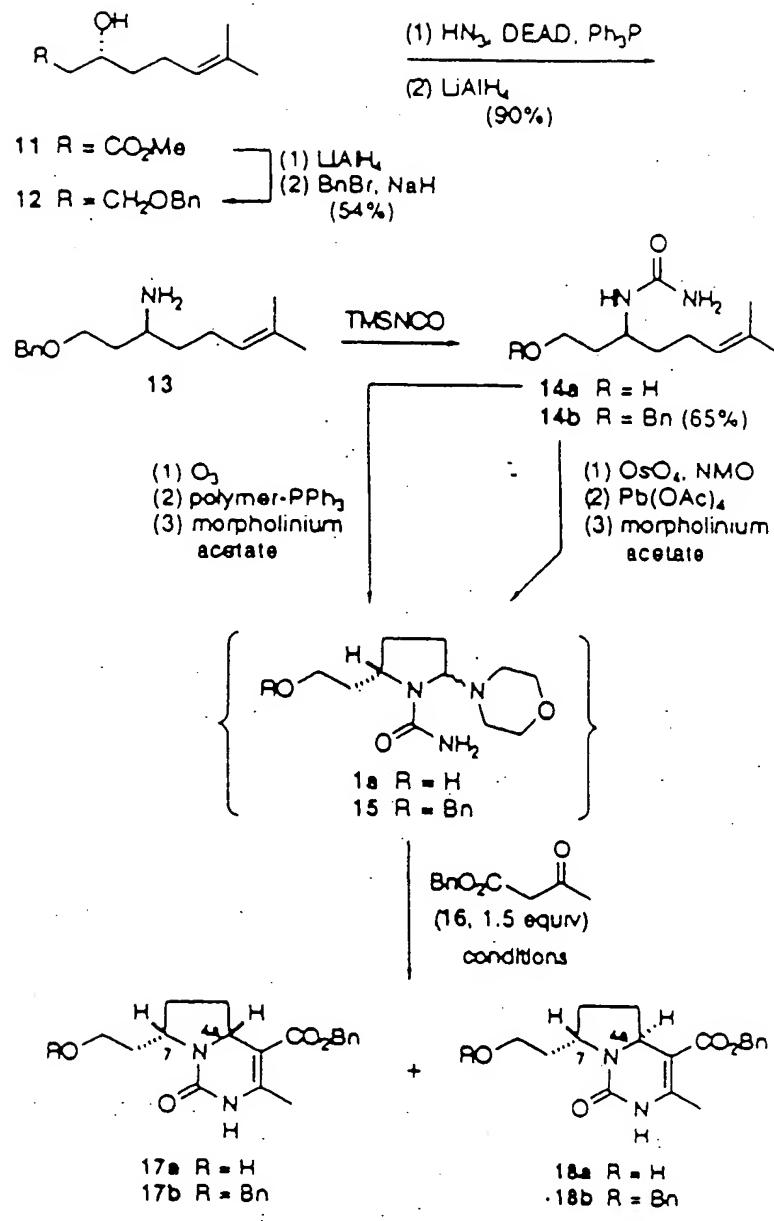


FIGURE .3



substrate	reaction conditions	17:18 (yield) ^a
1a	morpholinium acetate (1.5 eq), $\text{CF}_3\text{CH}_2\text{OH}$, 60°C , 48 h	4:1 (80%)
15		4:1 (81%)
15	PPE, CH_2Cl_2 , 23°C , 48 h	1:4 (60%)

^a Combined overall yield of 17 and 18 from 14.

FIGURE 4

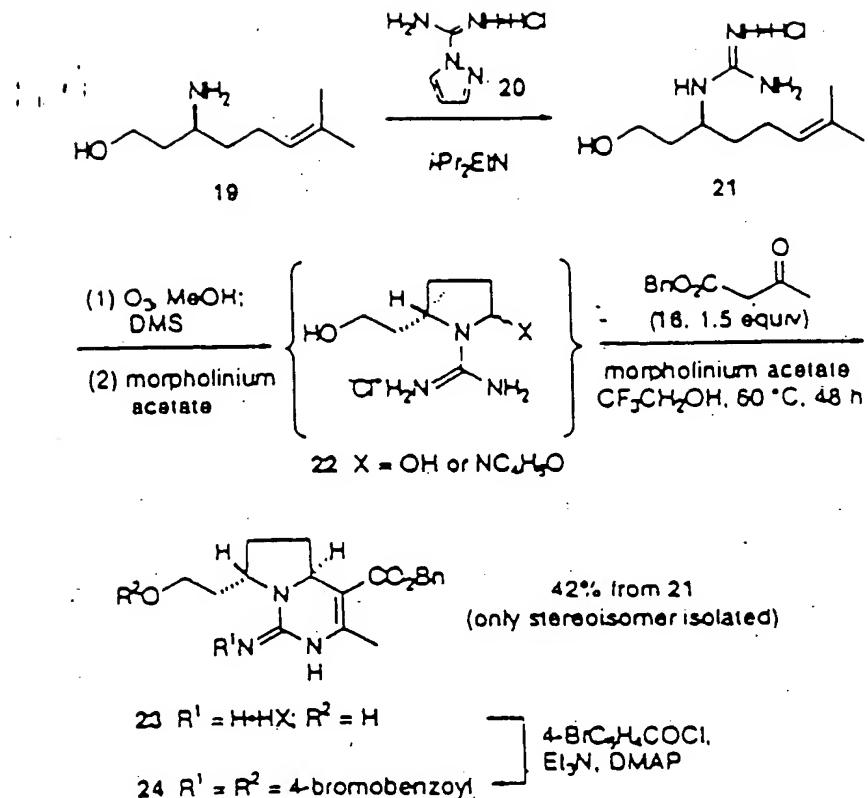
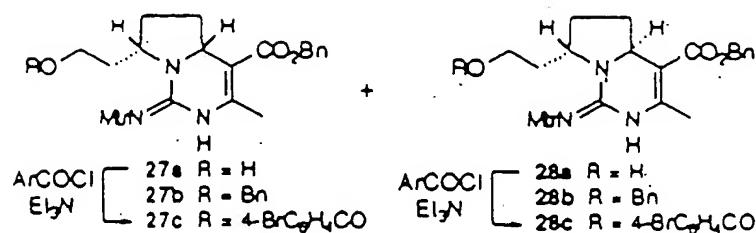
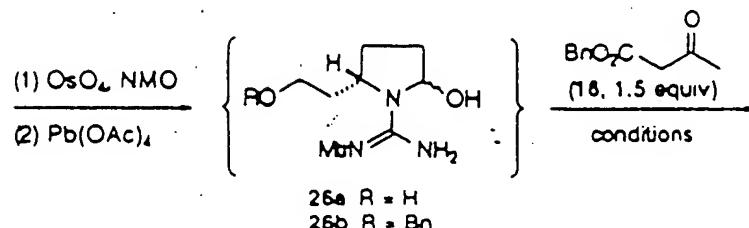
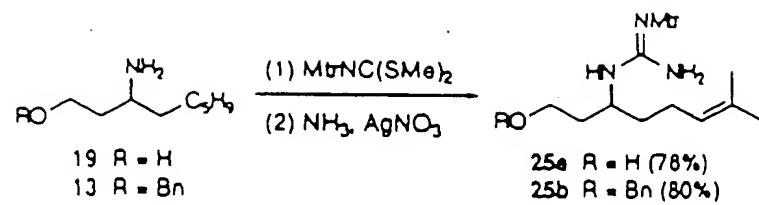


FIGURE 5



substrate	reaction conditions	27:28 (yield) ^a
26a	morpholinium acetate (1.5 eq),	6:1 (61%)
26b	CF3CH2OH, 60 °C, 48 h	7:1 (84%)
26b	PPE, CH2Cl2, 23 °C, 48 h	1:20 (61%)

^a Combined overall yield of 27 and 28 from 25.

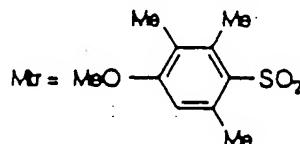


FIGURE 6

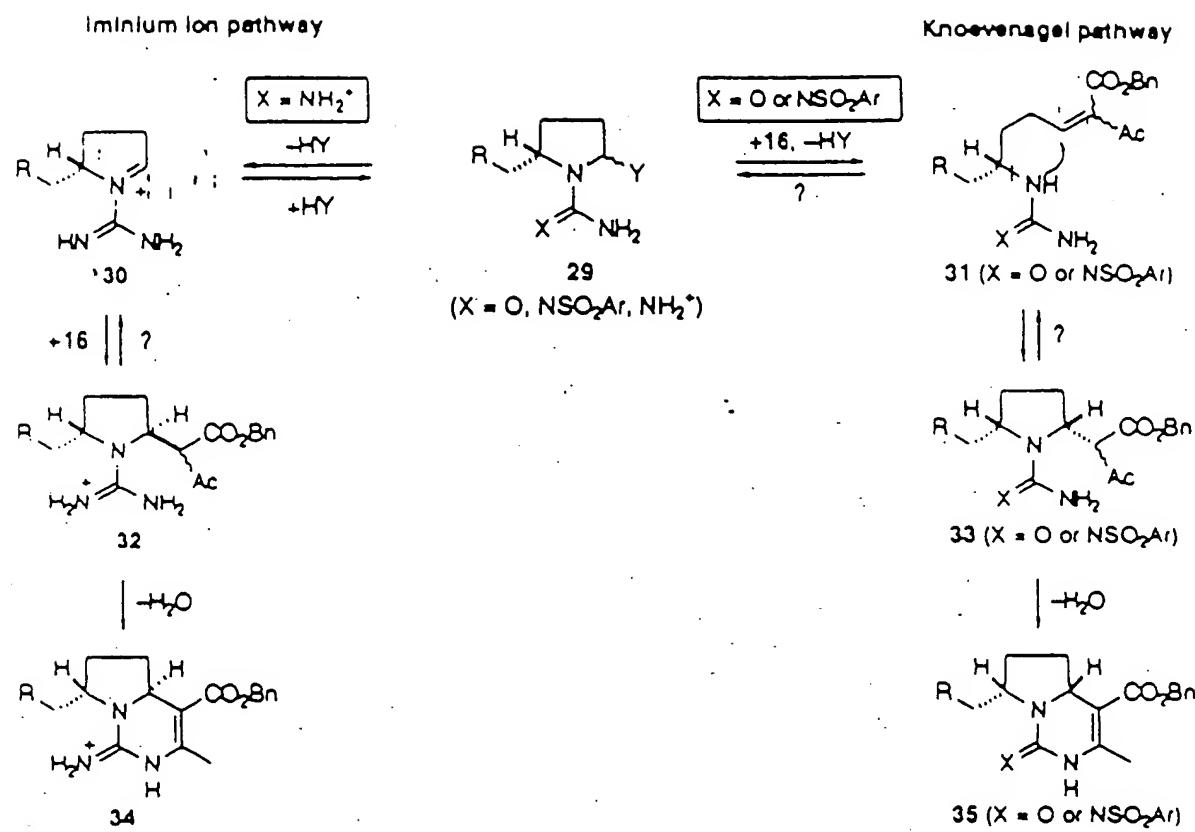


FIGURE 7

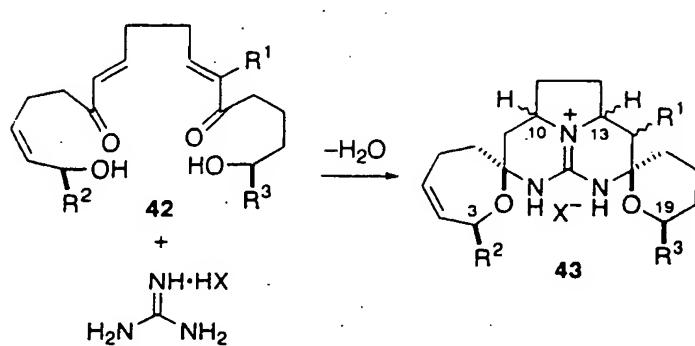
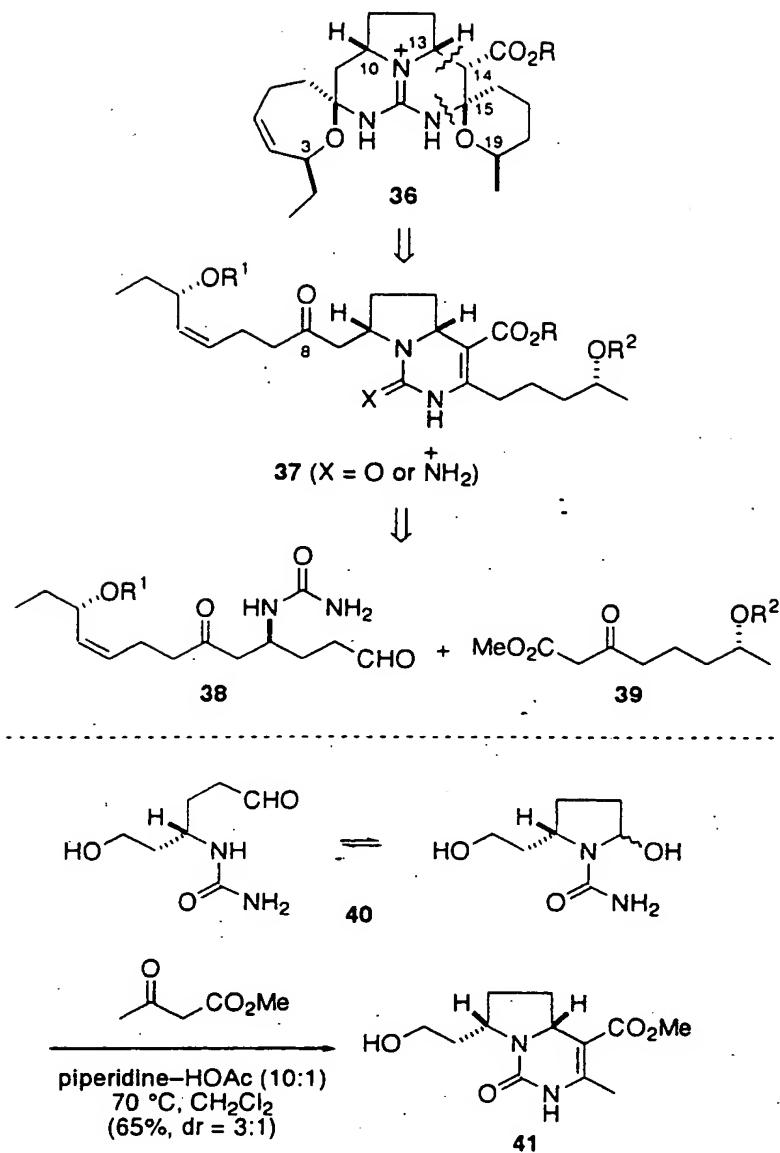


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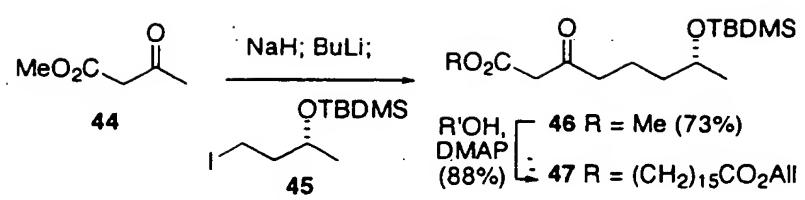


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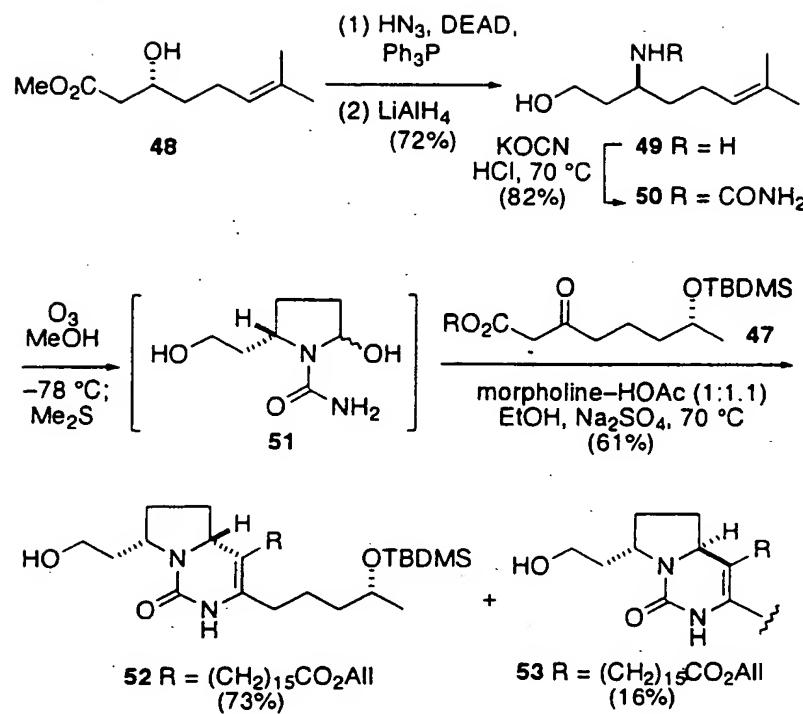


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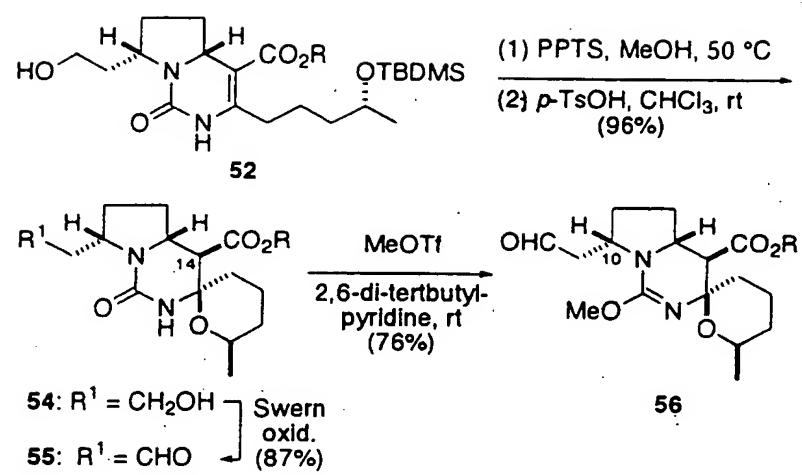


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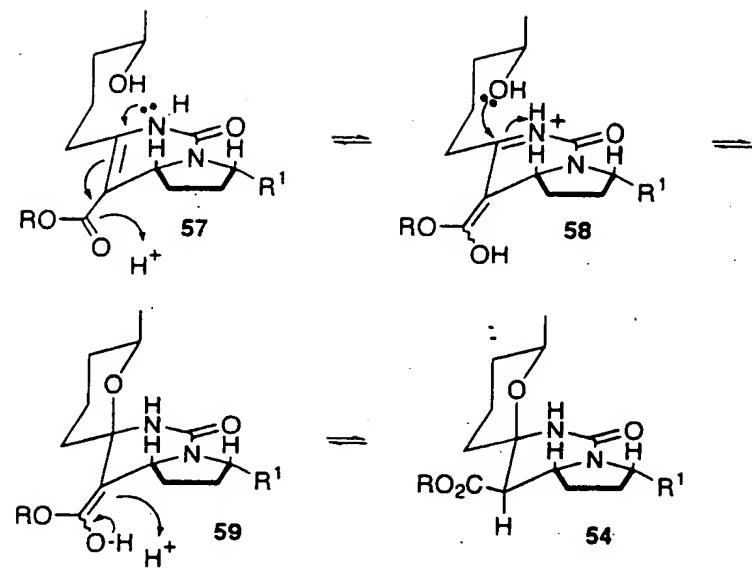


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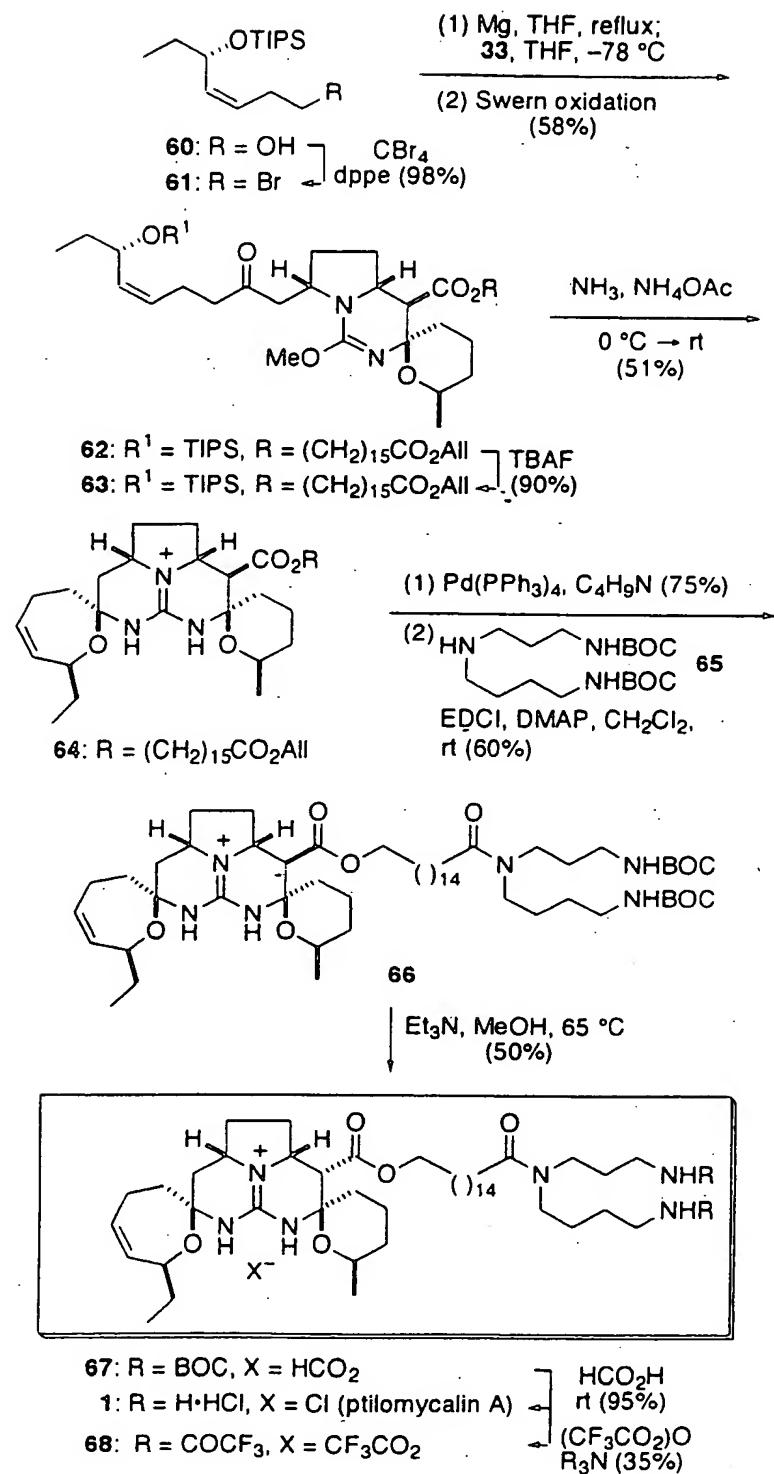


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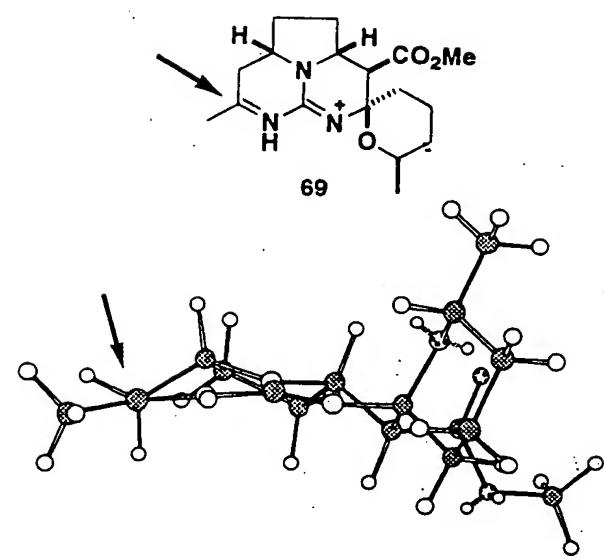


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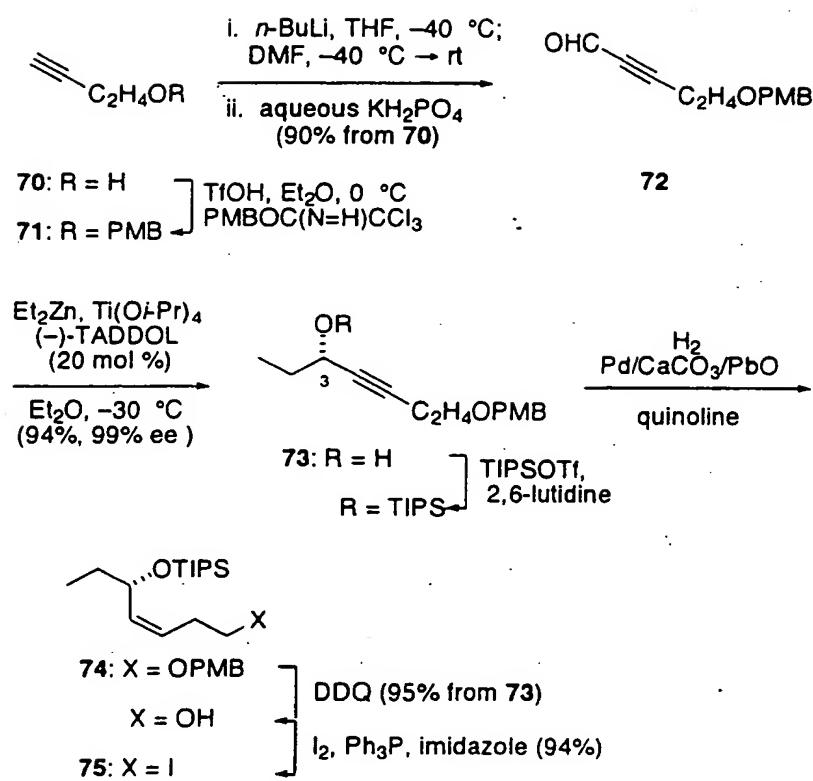


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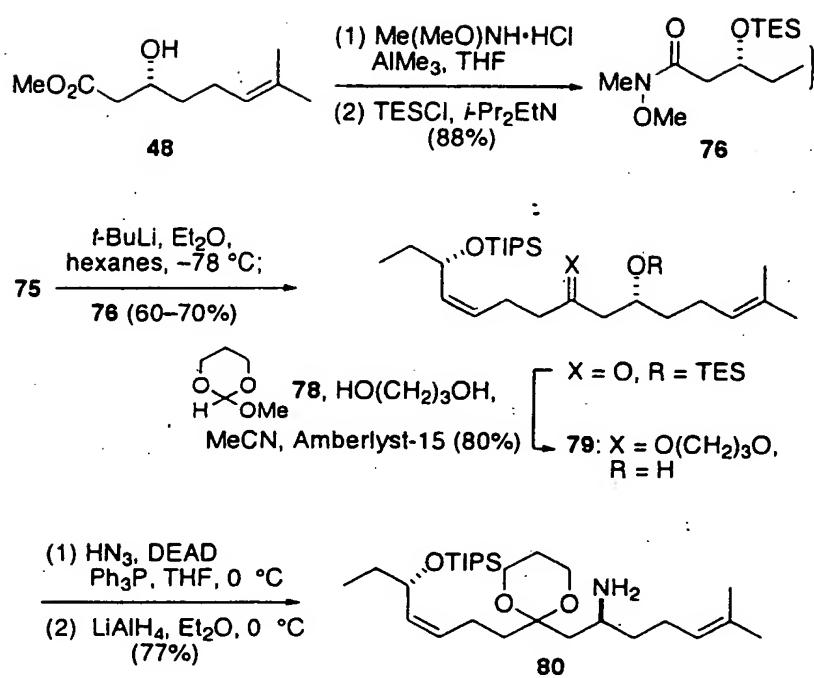


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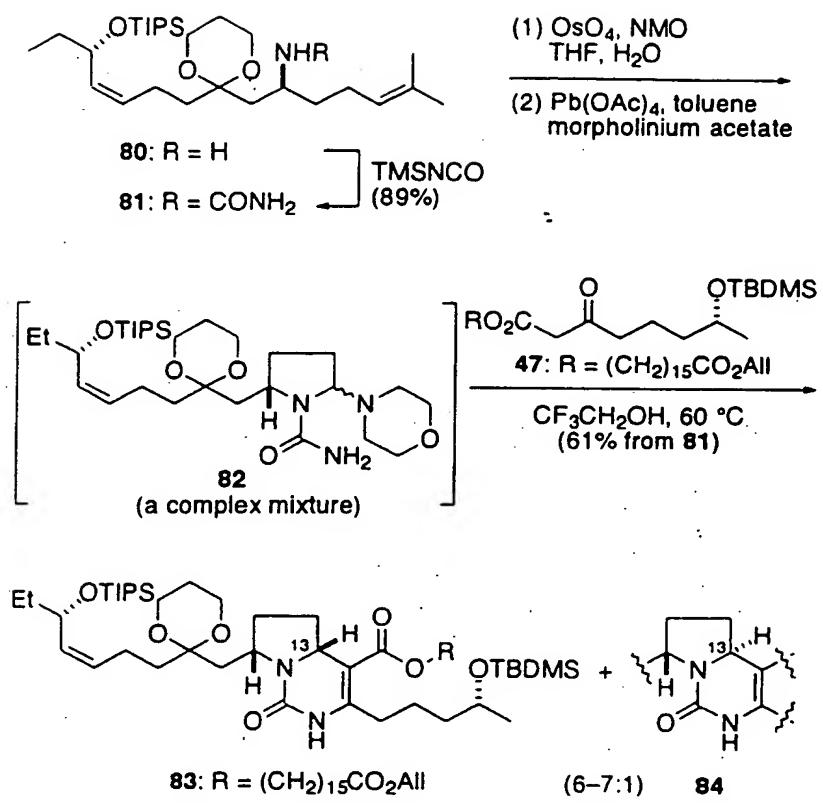


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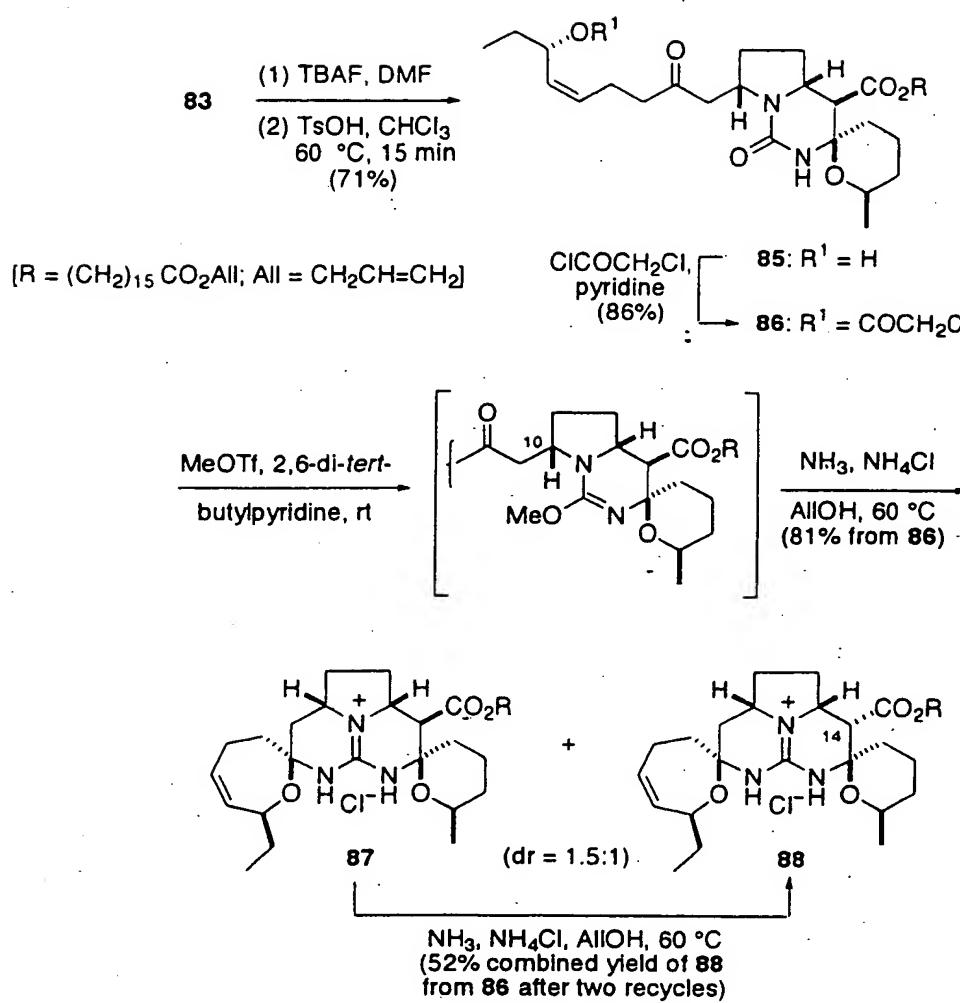


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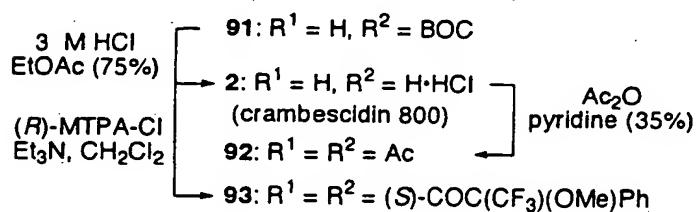
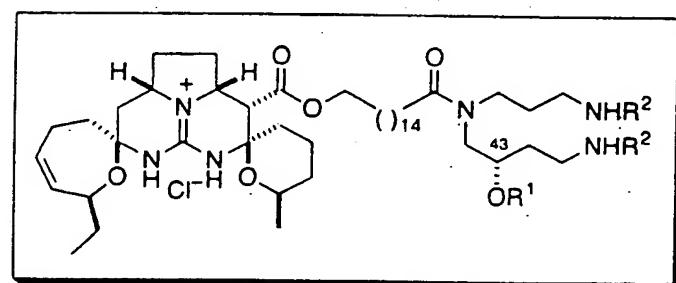
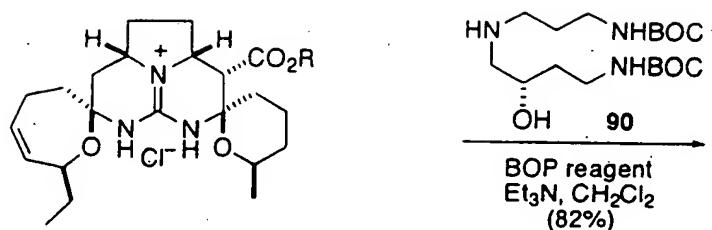
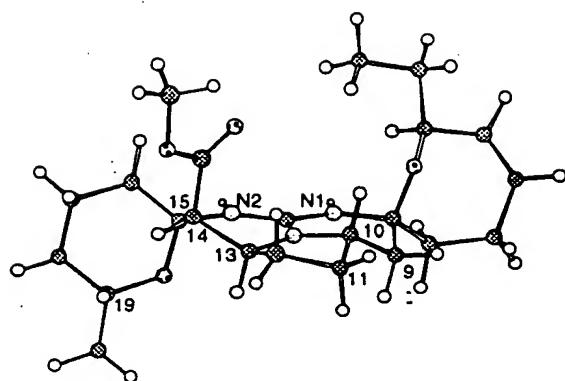
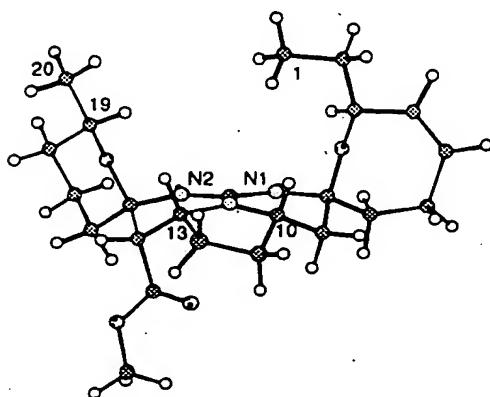


Figure 19



13,14,15-isocrambescidin core



crambescidin/ptilomycalin A core

Figure 20

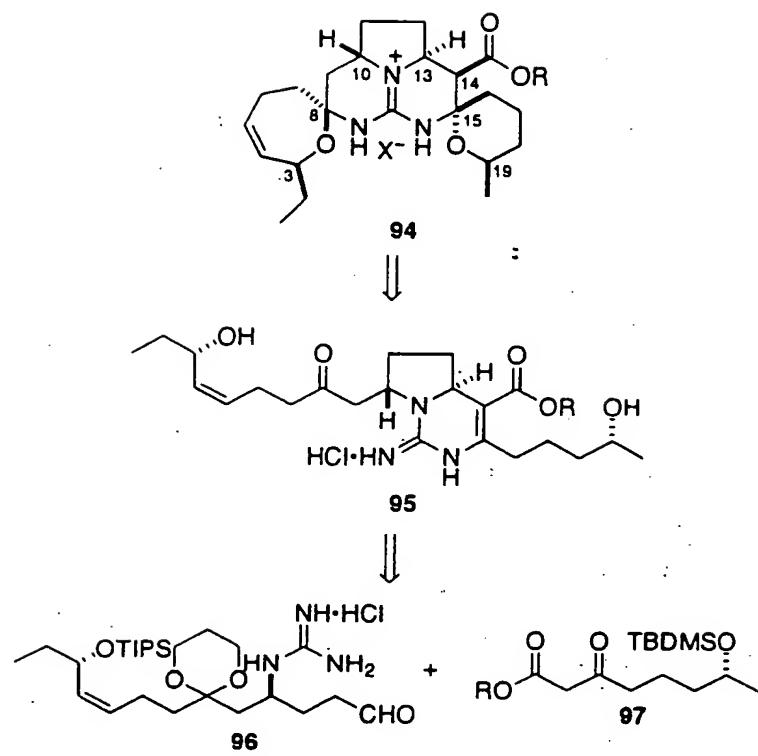


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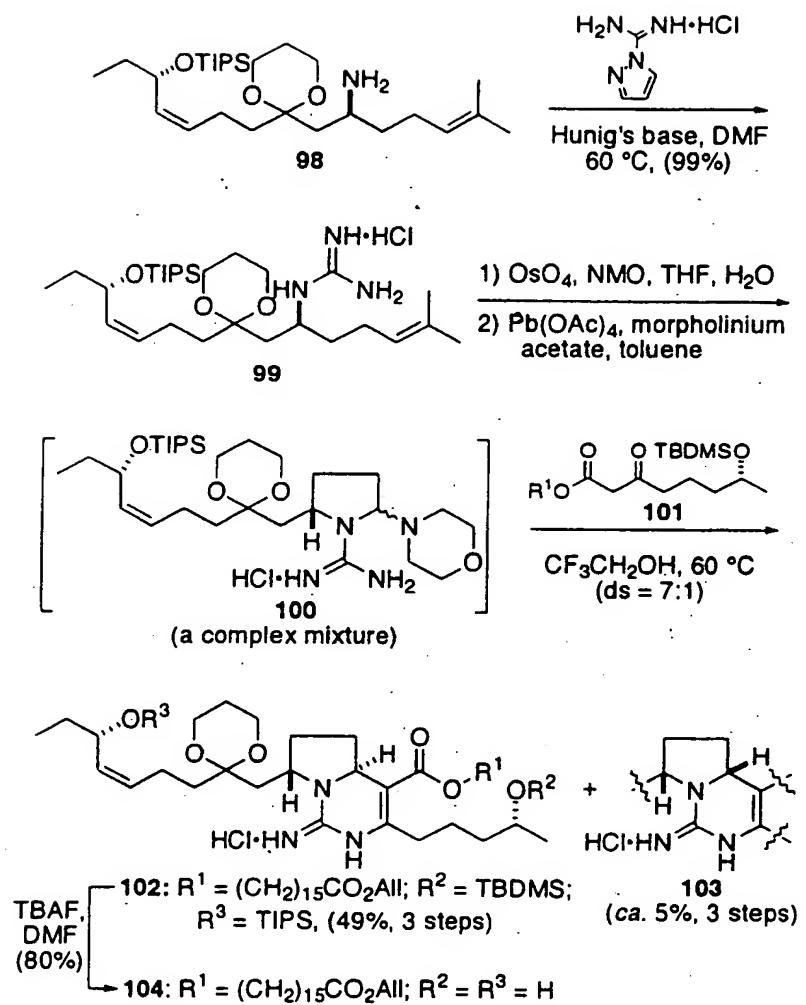


Figure 22

$R = (CH_2)_{15}CO_2All$

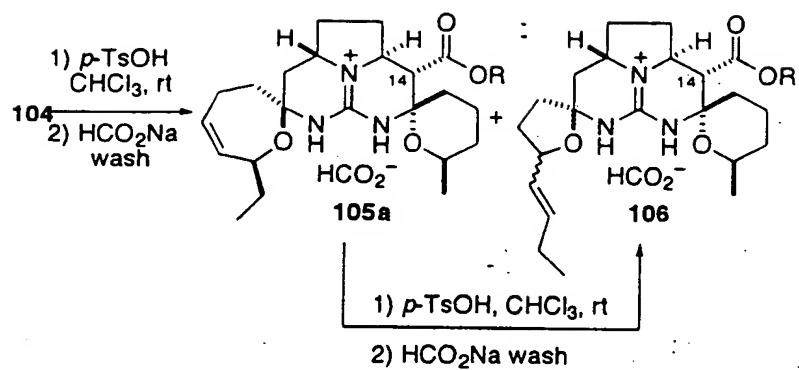


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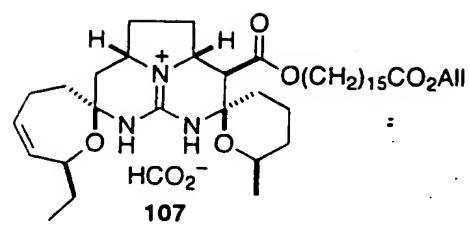
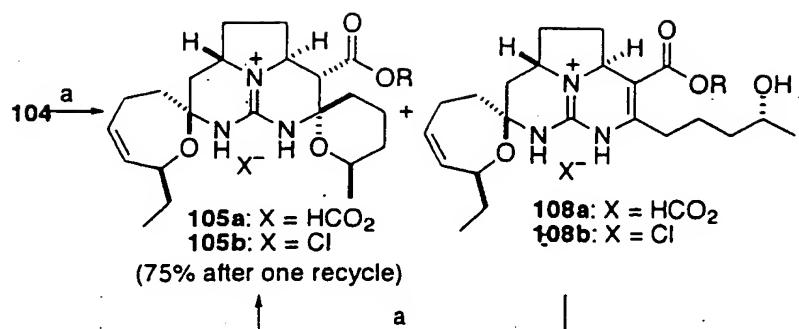


Figure 24

$R = (CH_2)_{15}CO_2Al$



^aReagents: (a) PPTS, $CHCl_3$, 90 °C, 24 h; HCO_2 Na wash
or 0.1 N HCl wash

Figure 25

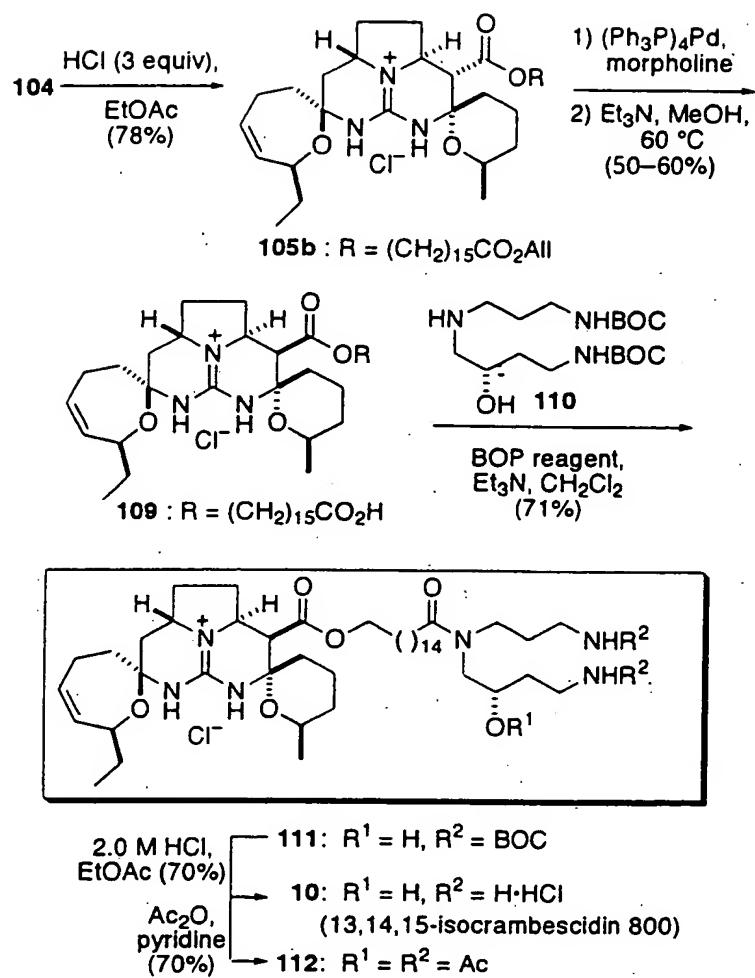


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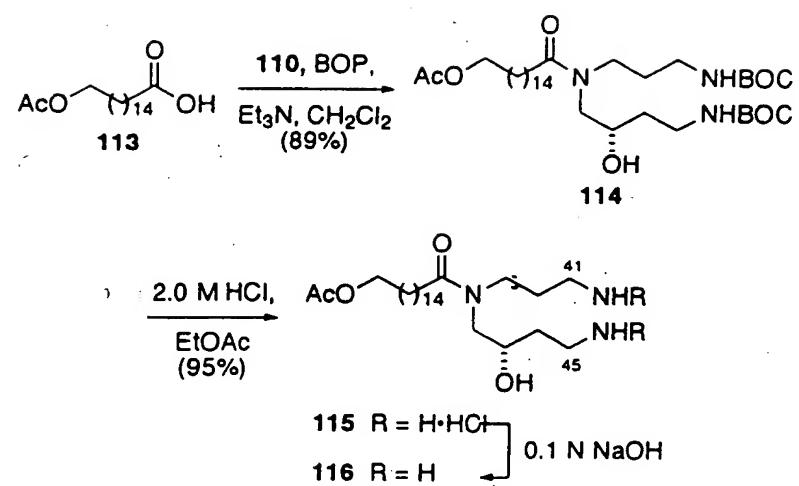


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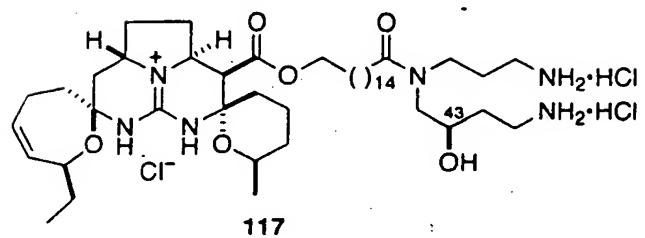
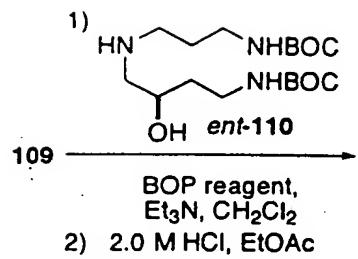
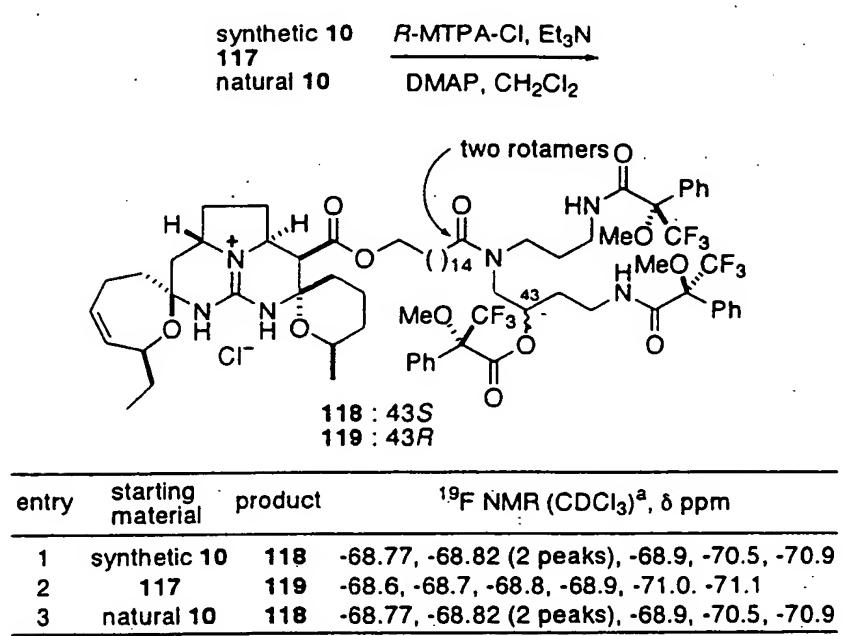


Figure 28



^aDue to rotamers about the C38 amide, there are six peaks in the ^{19}F NMR spectra.

Figure 29

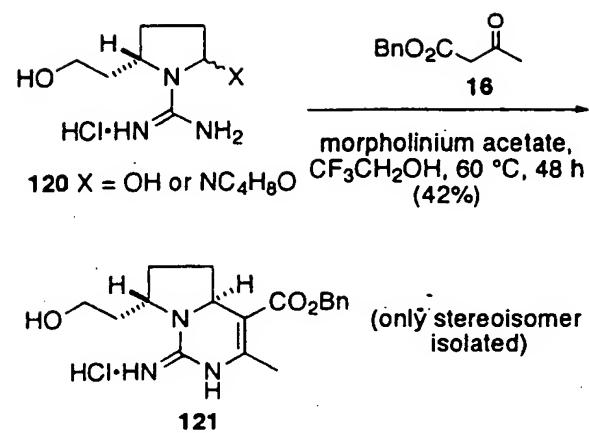
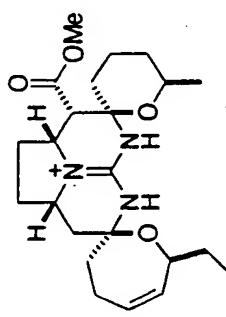
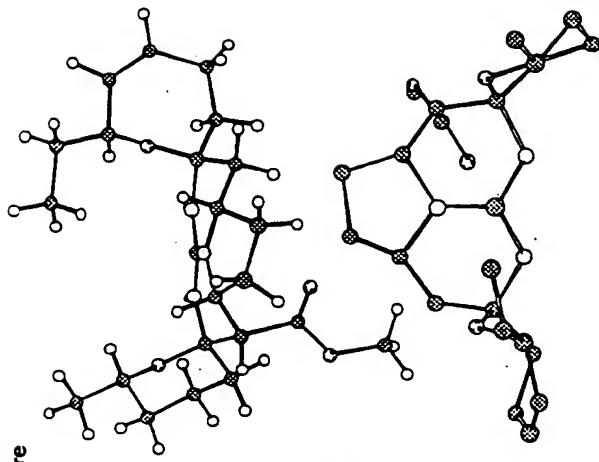
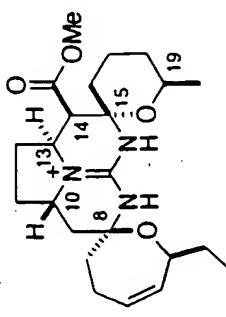
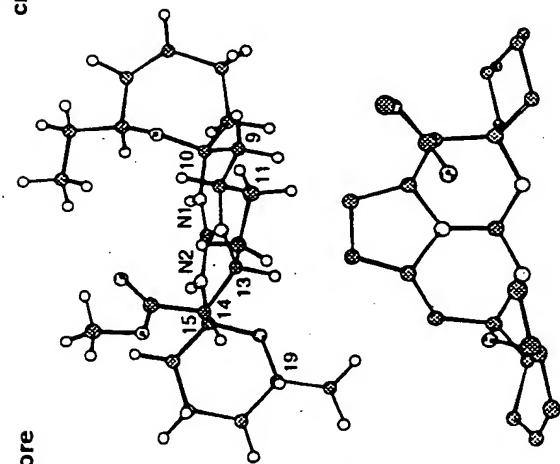


Figure 30

crambescidin/ptiliomycalin A core



13,14,15-Isocrambescidin core



13,15-epicrambescidin core

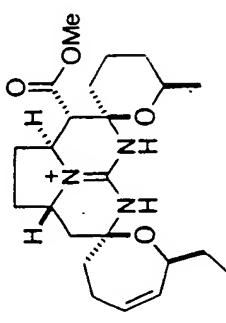
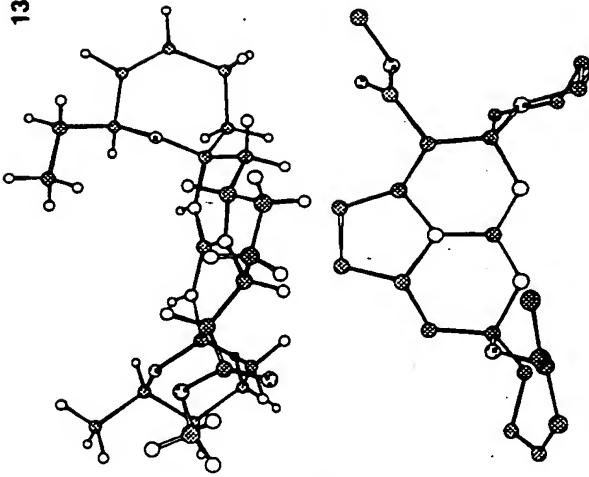
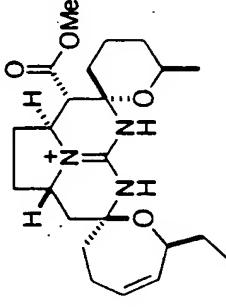
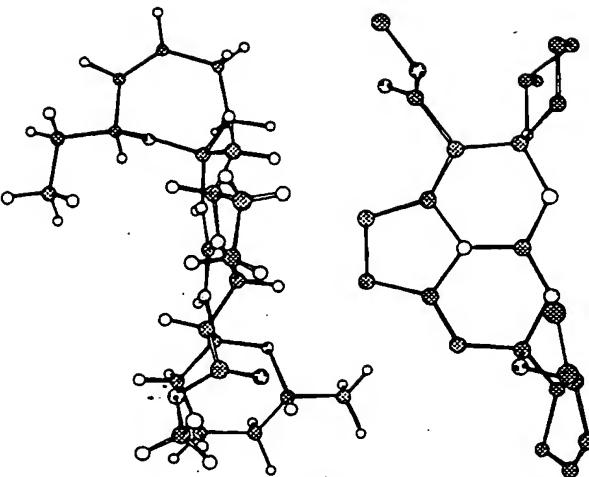


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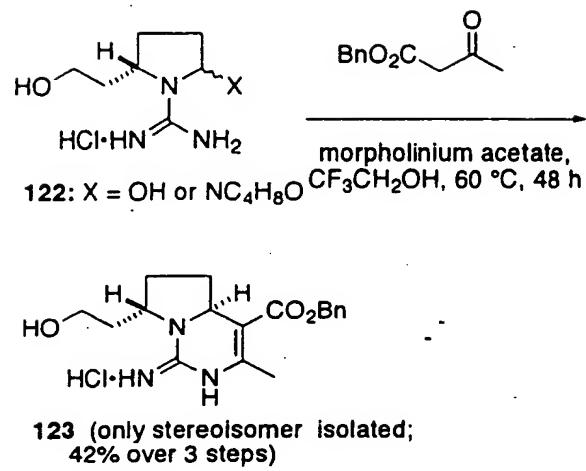


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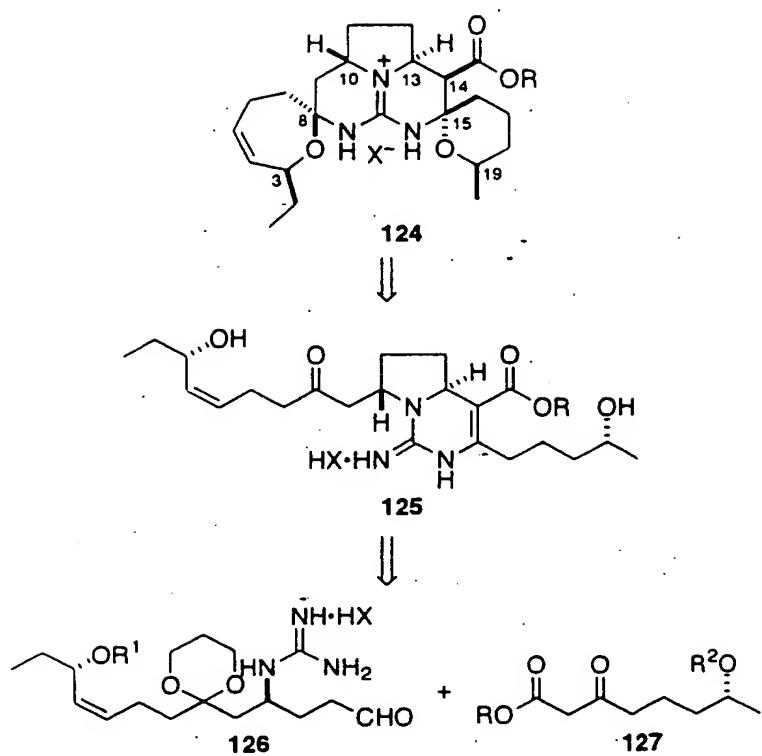


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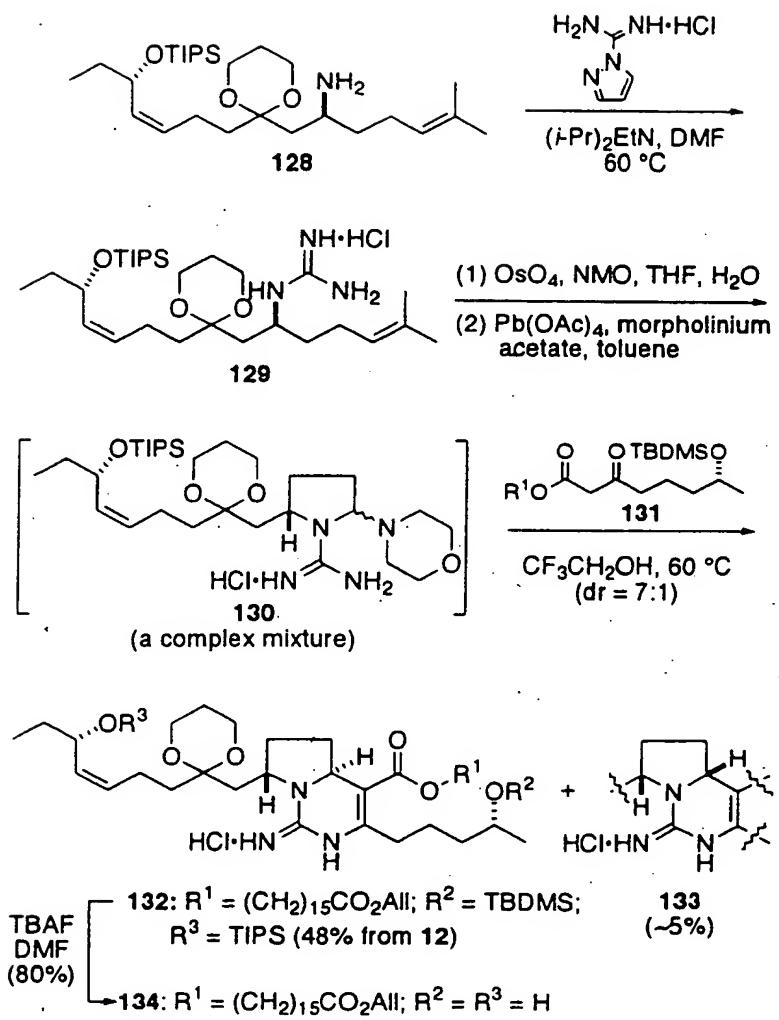


Figure 34

$R = (CH_2)_{15}CO_2All$

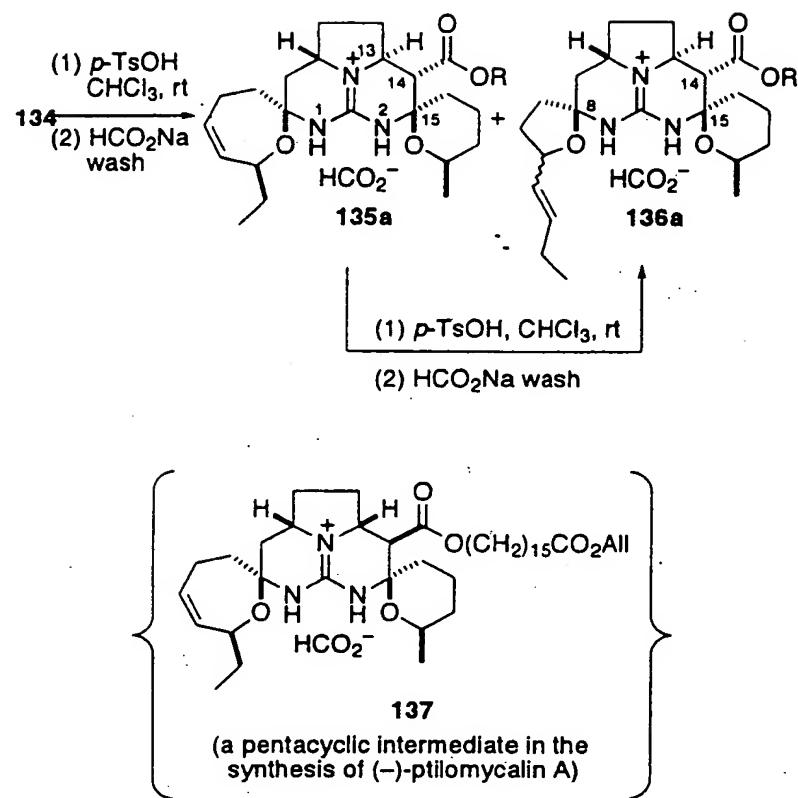
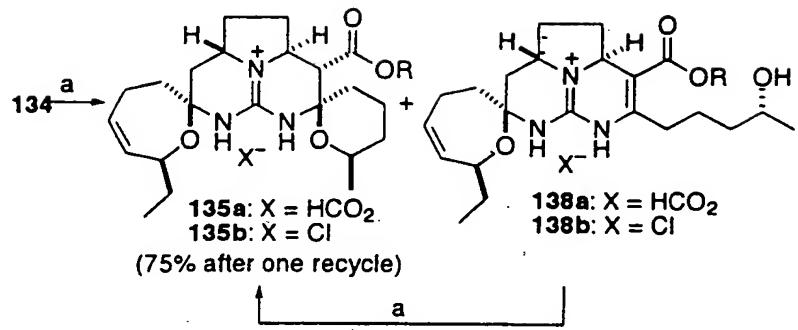


Figure 35

$R = (CH_2)_{15}CO_2All$



^aReagents: (a) PPTS, $CHCl_3$, $90^\circ C$, 24 h; HCO_2Na wash or 0.1 N HCl wash

Figure 36

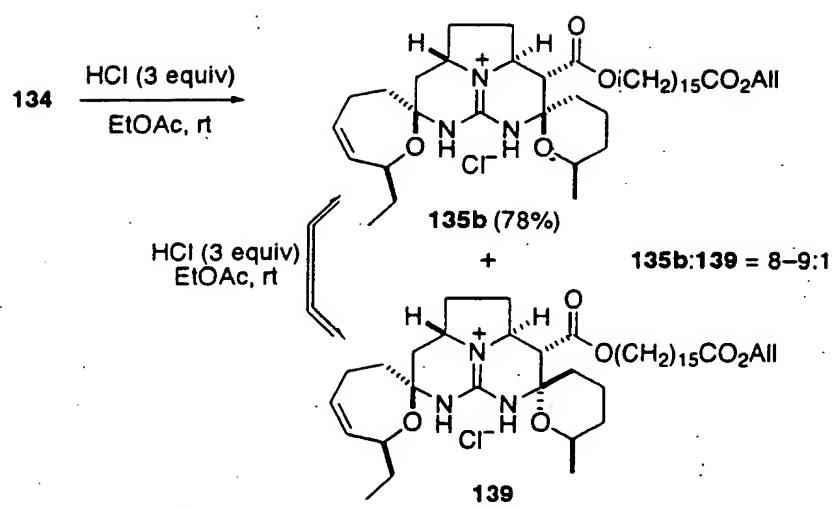
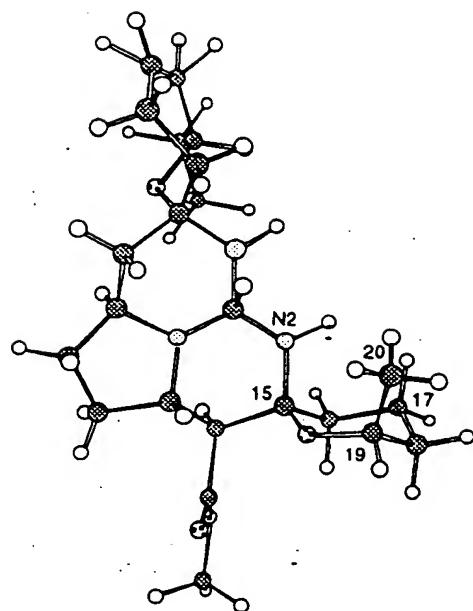


Figure 37

A



B

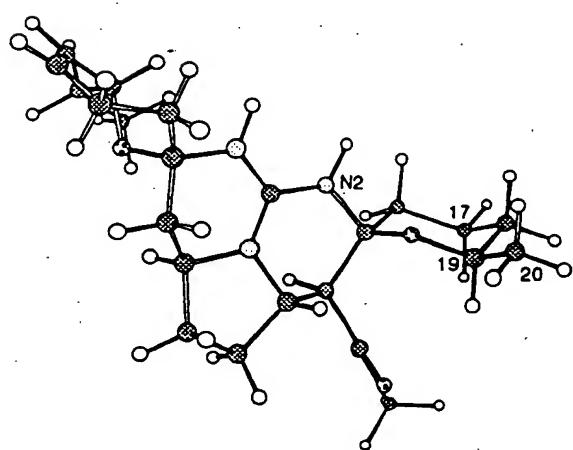
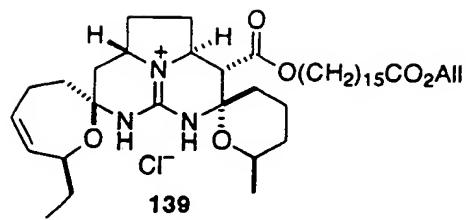
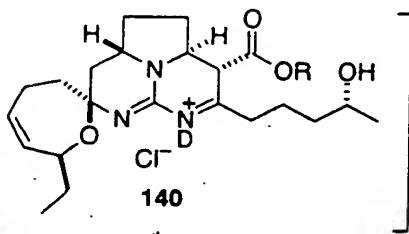


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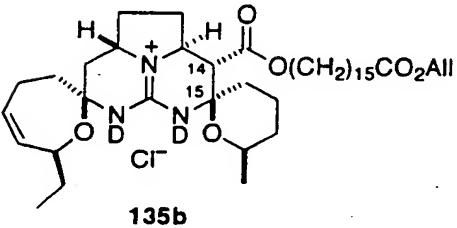
139

DCI, EtOAc
rt, 24 h



140

no deuterium
incorporation
at C14



135b

Figure 39

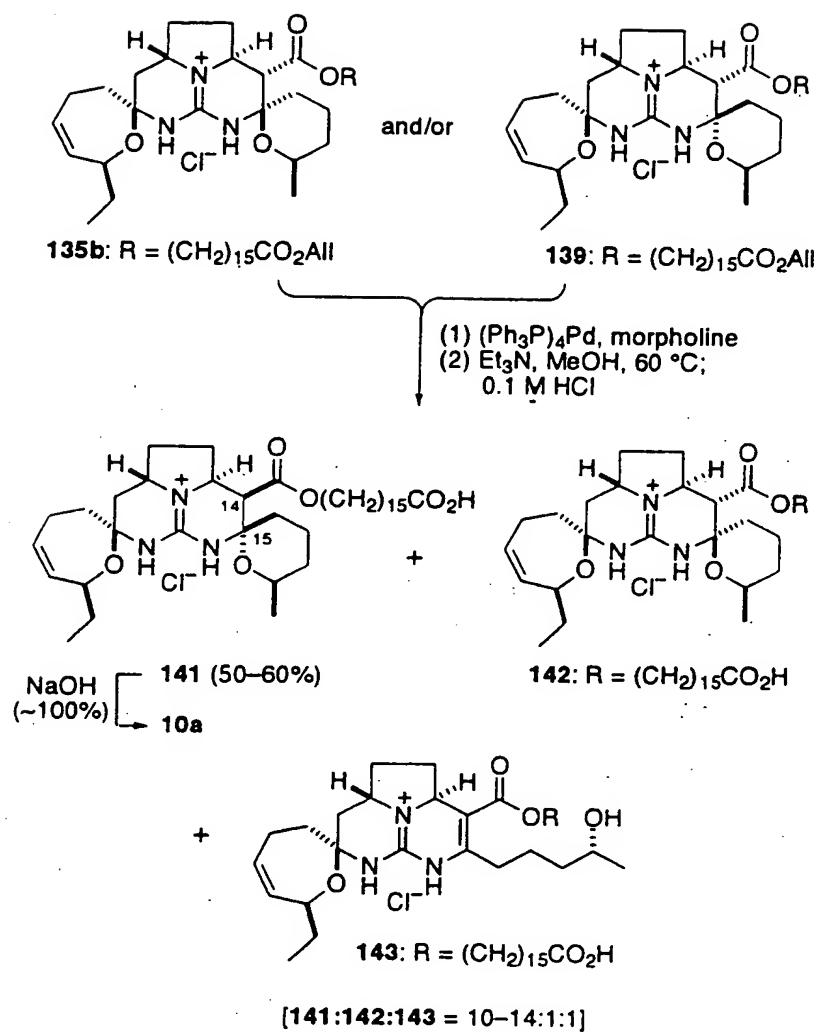


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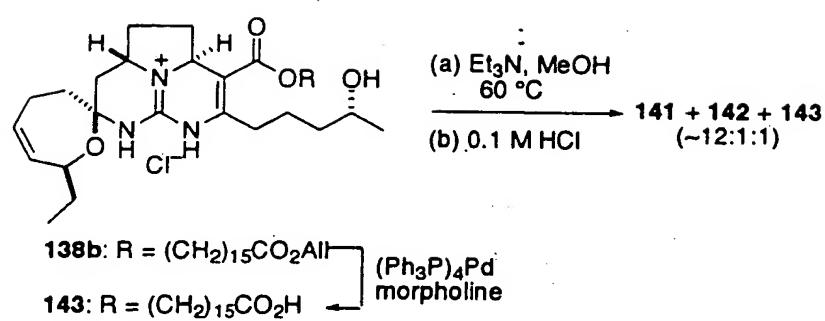


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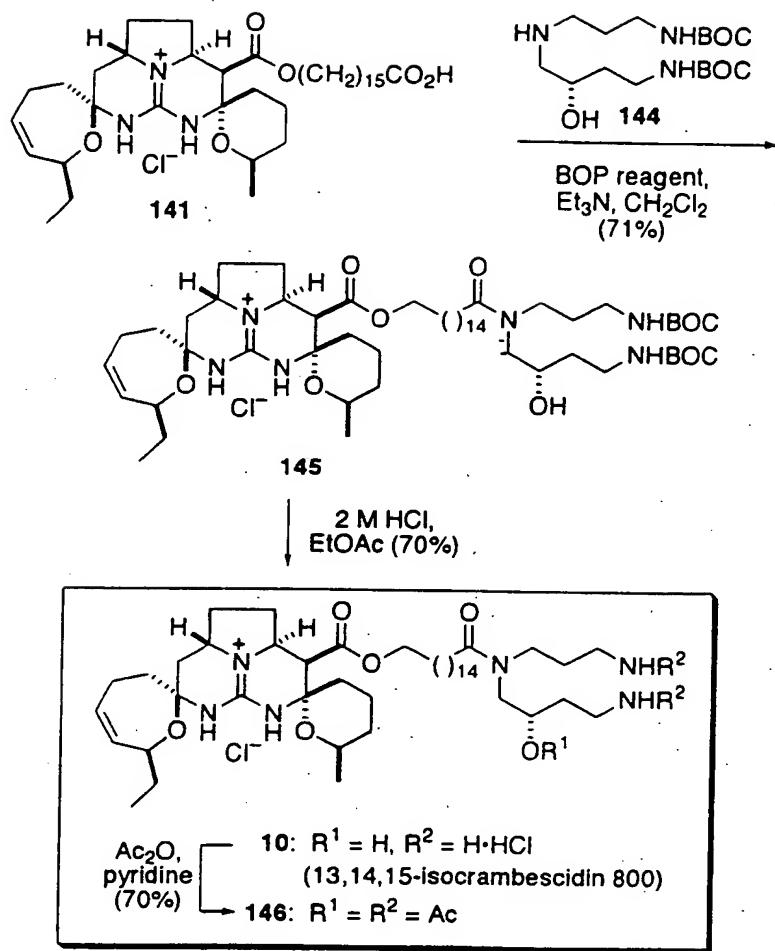


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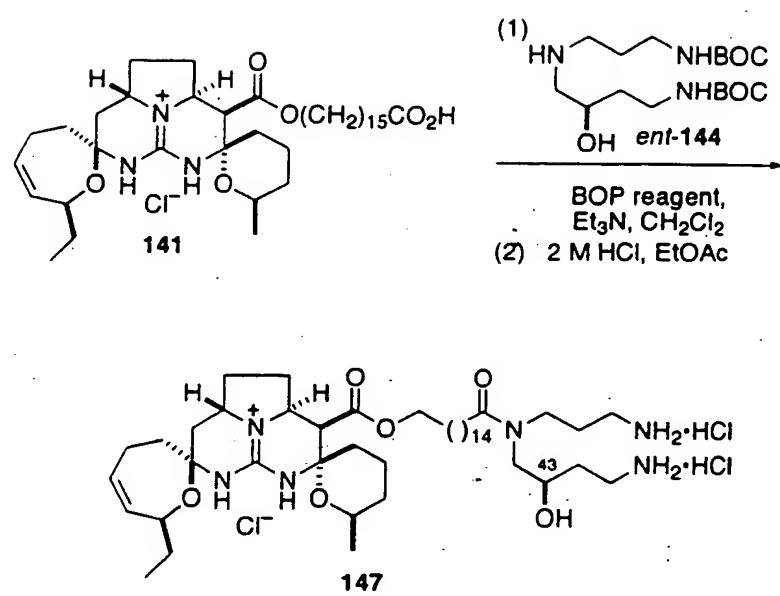
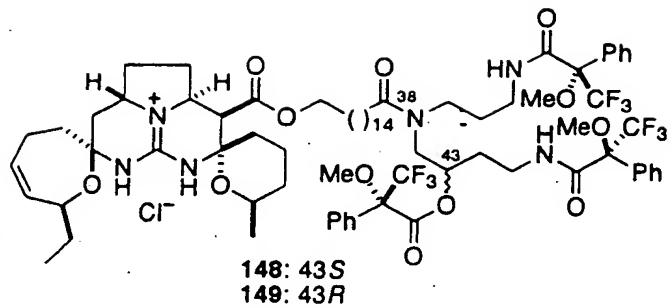


Figure 43



entry	starting material	product	^{19}F NMR (CDCl_3) ^a , δ ppm
1	synthetic 10	148	-68.77, -68.82 (2 peaks), -68.9, -70.5, -70.9
2	147	149	-68.6, -68.7, -68.8, -68.9, -71.0, -71.1
3	natural 10	148	-68.77, -68.82 (2 peaks), -68.9, -70.5, -70.9

^aDue to rotamers about the C38 amide bond on the NMR time scale, six peaks are observed in the ^{19}F NMR spectra.

Figure 44

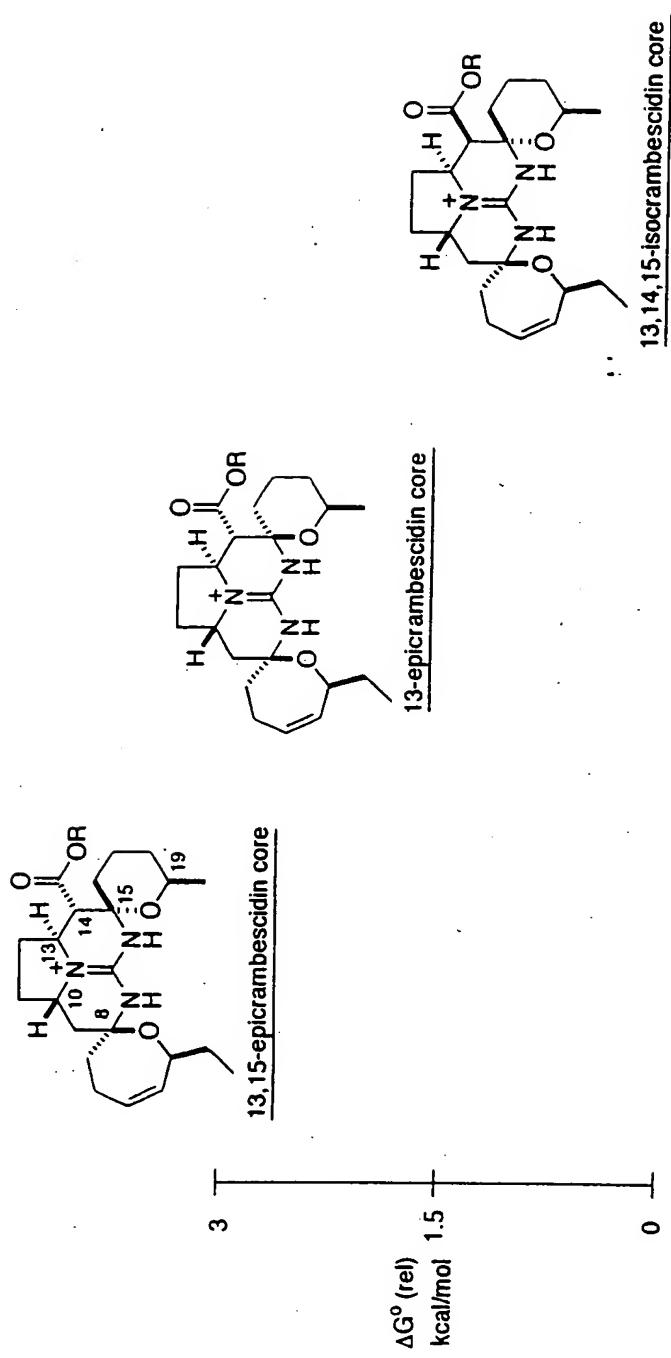


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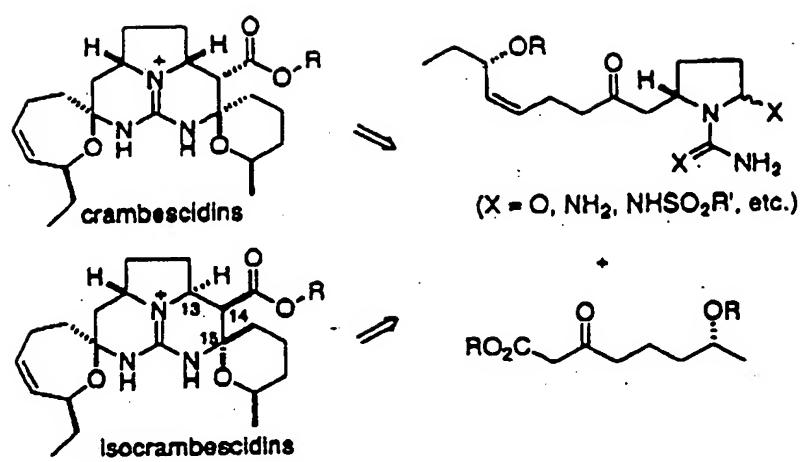


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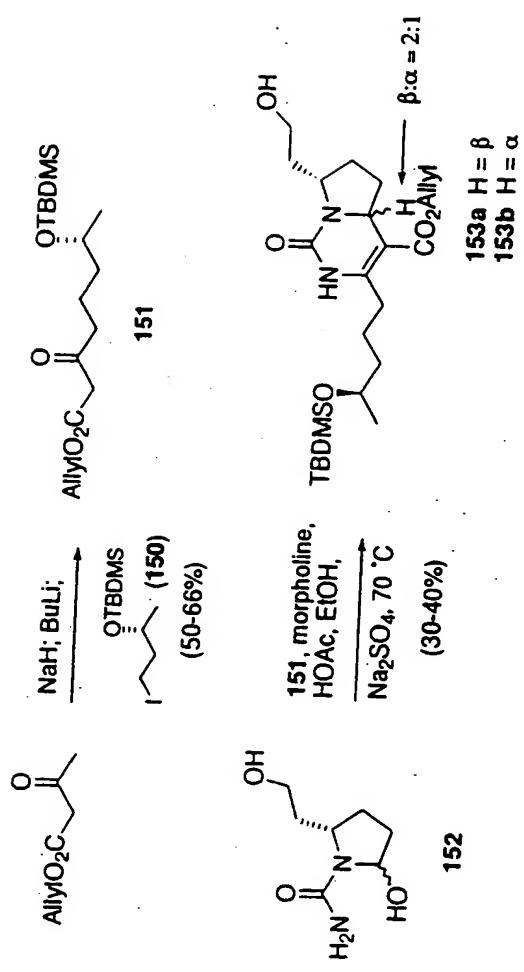


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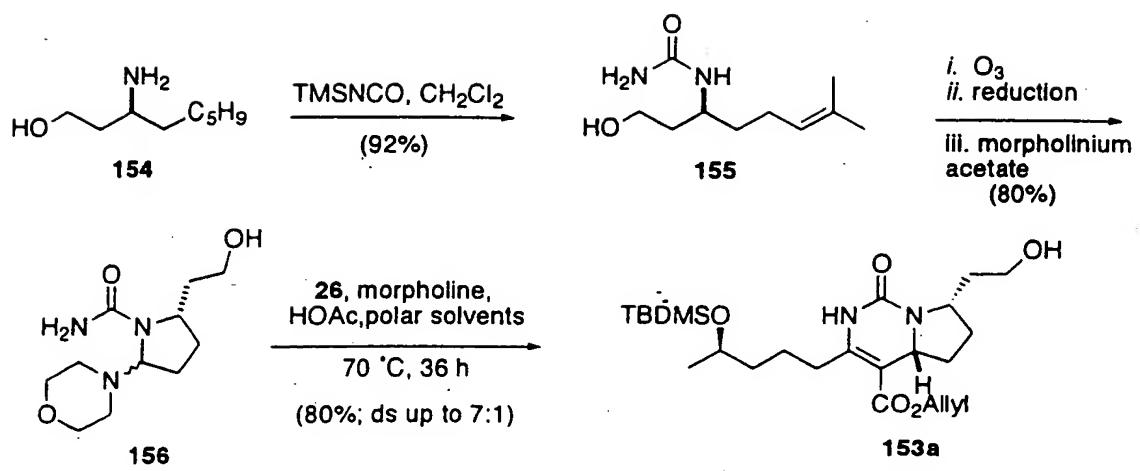


Figure 48

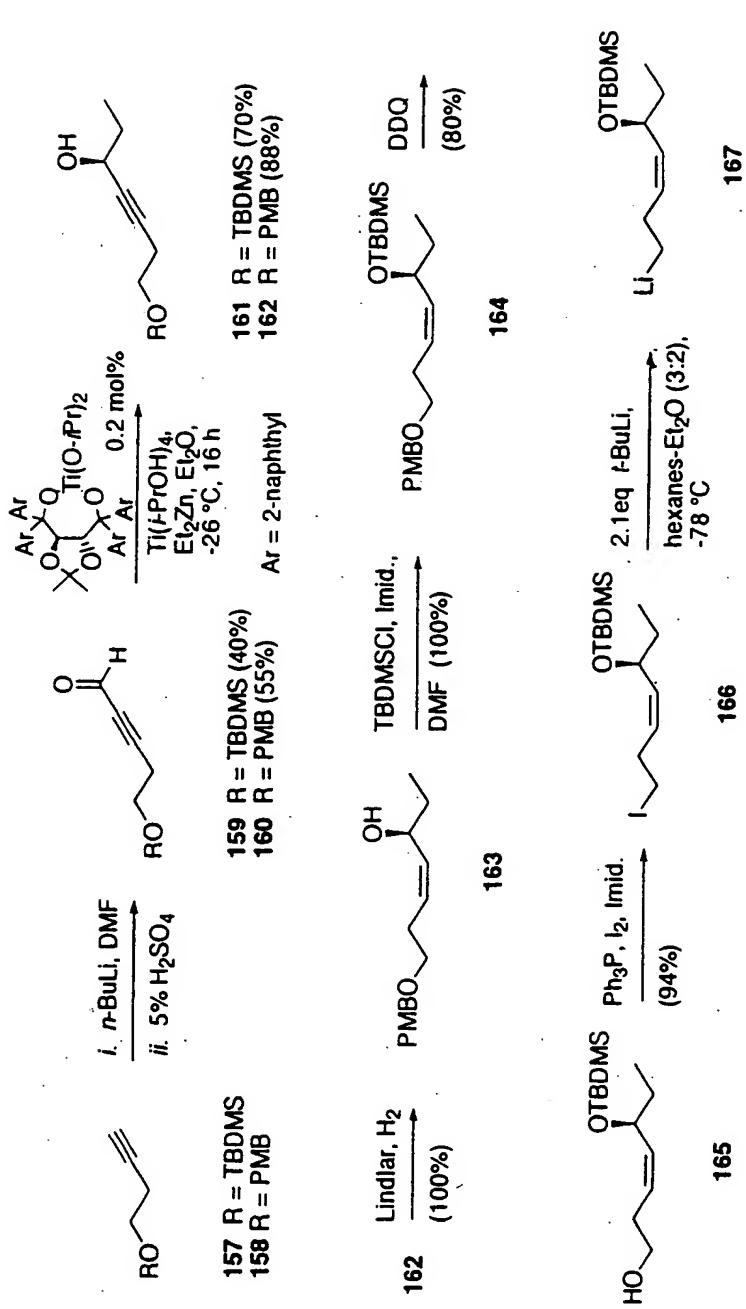


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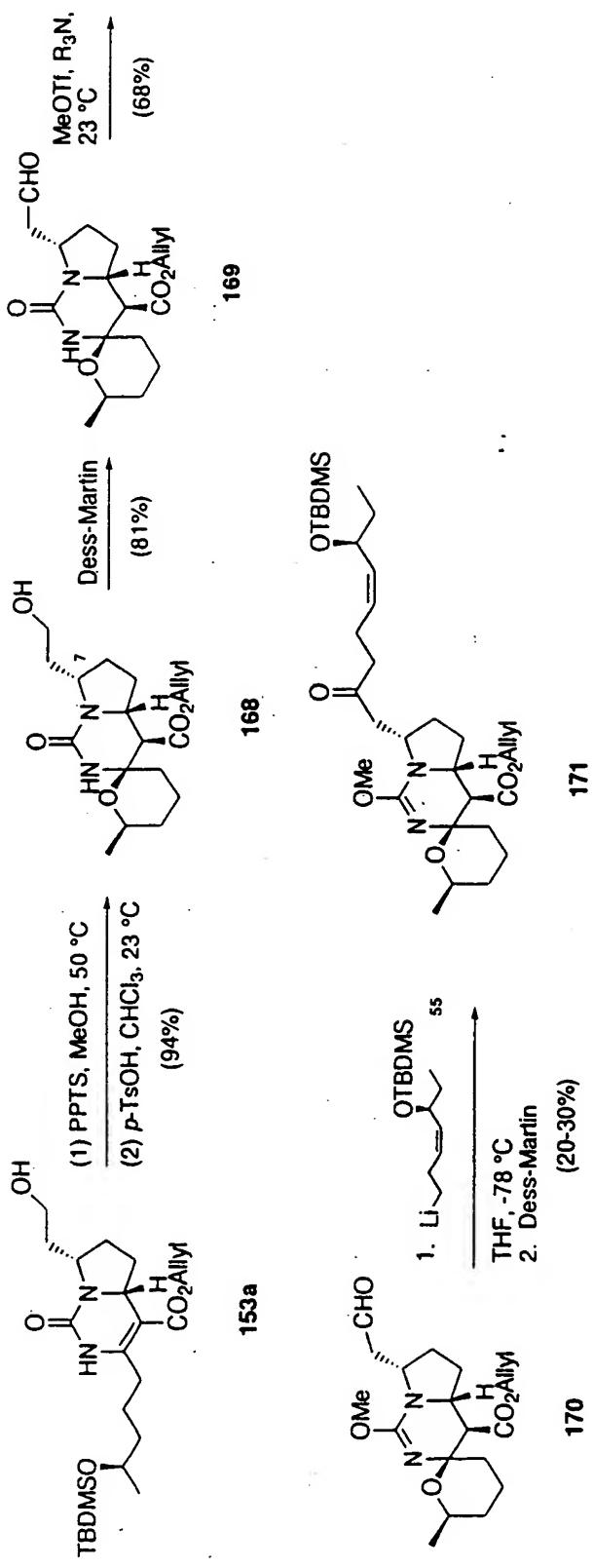


Figure 50

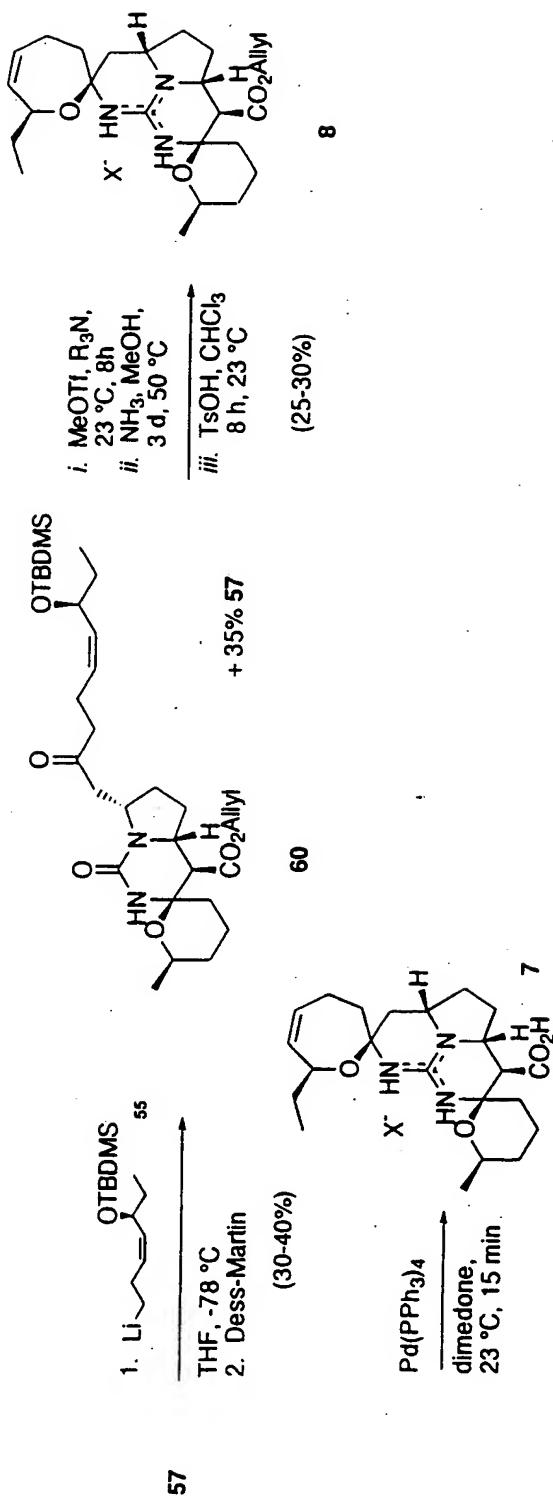


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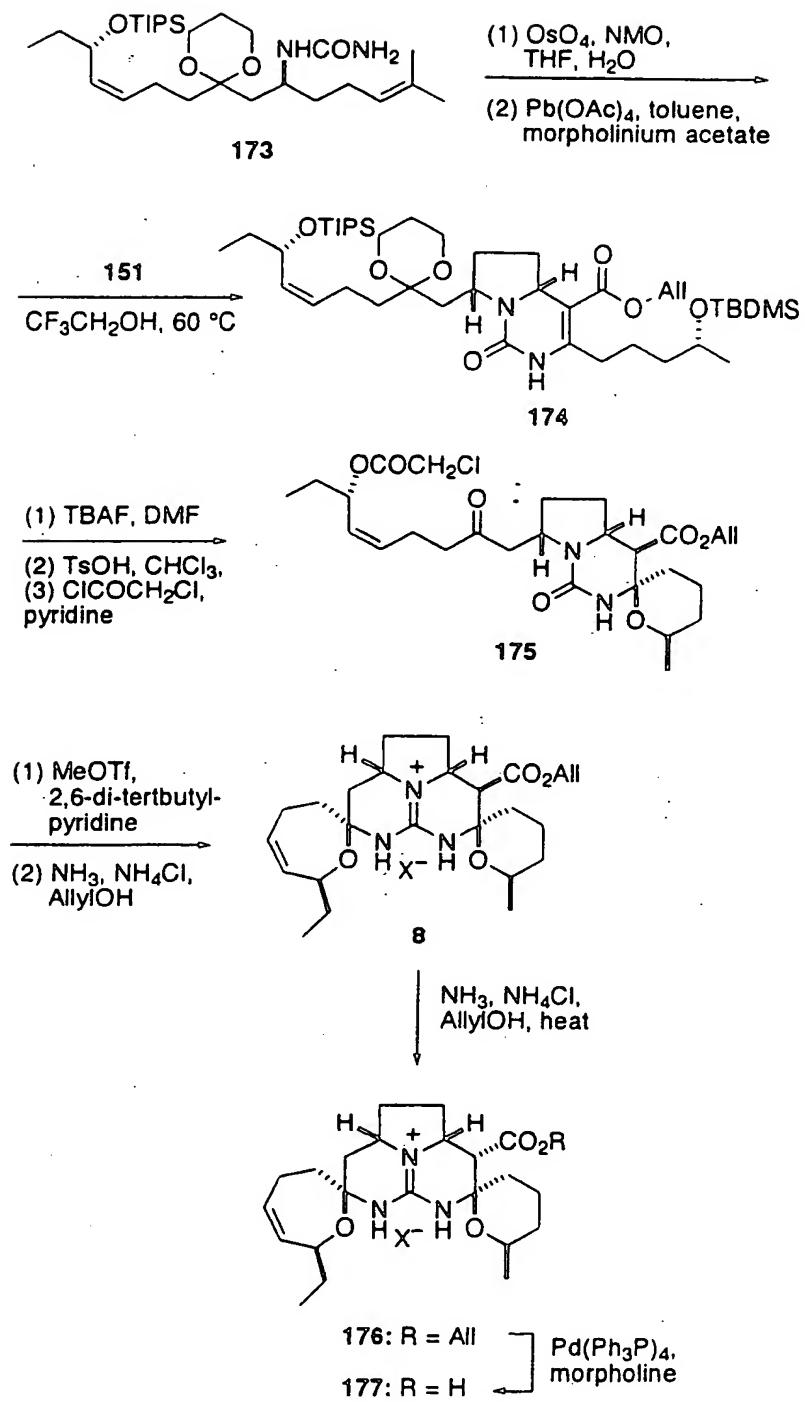


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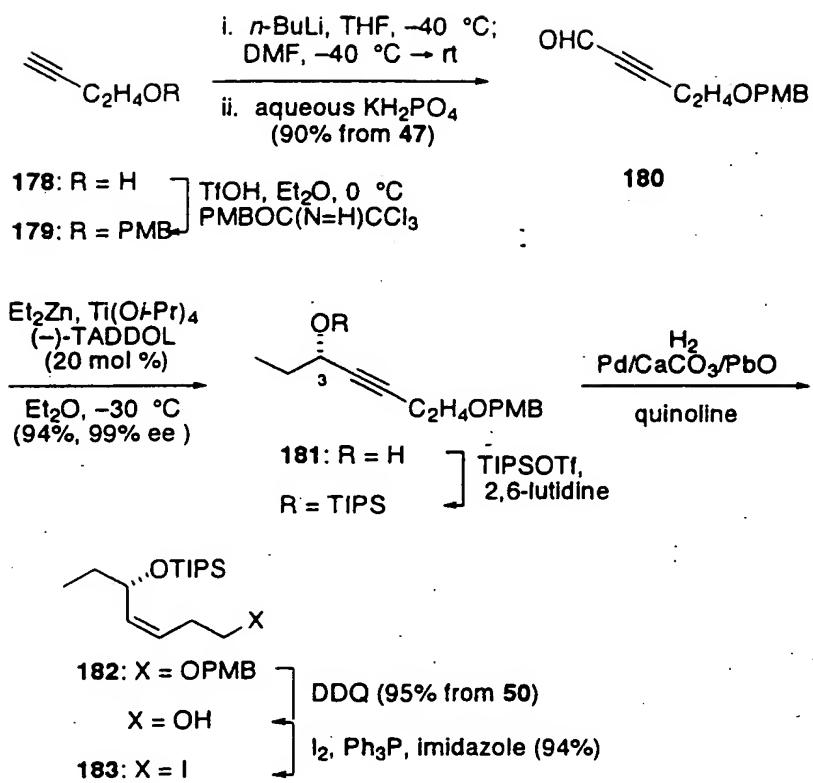


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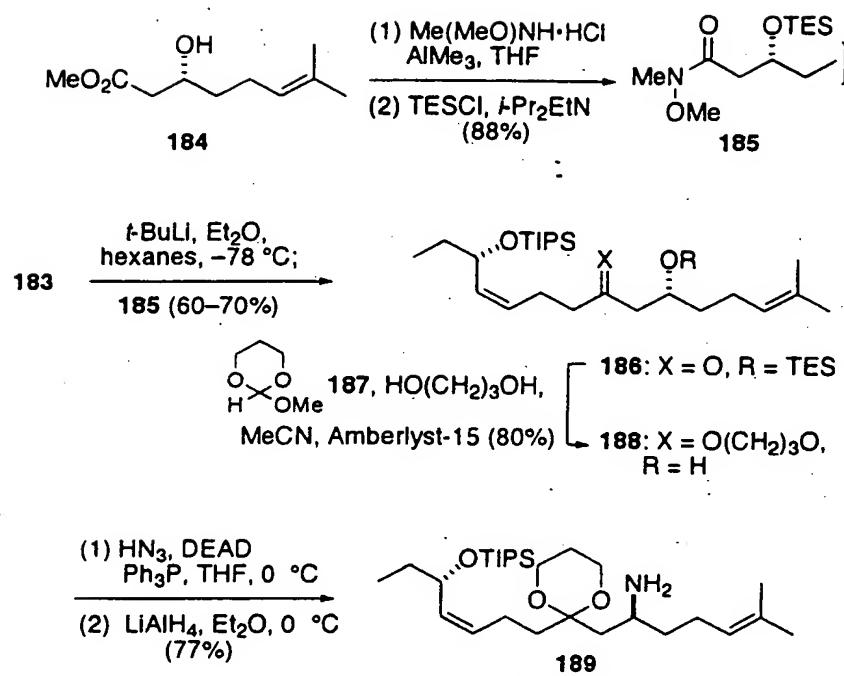


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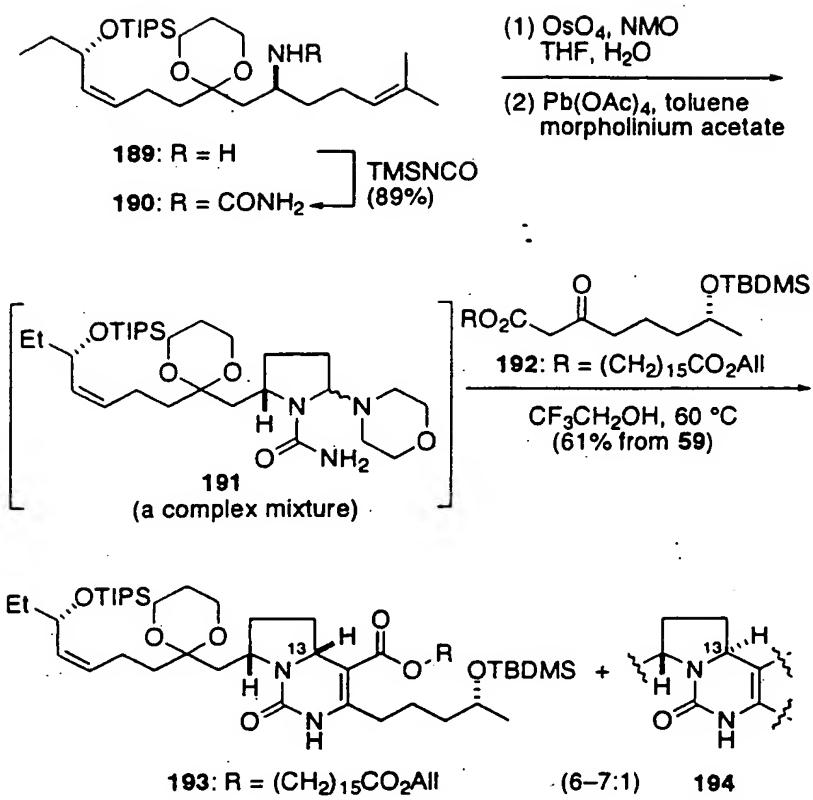


Figure 55

National Cancer Institute Developmental Therapeutics Program

Mean Graphs

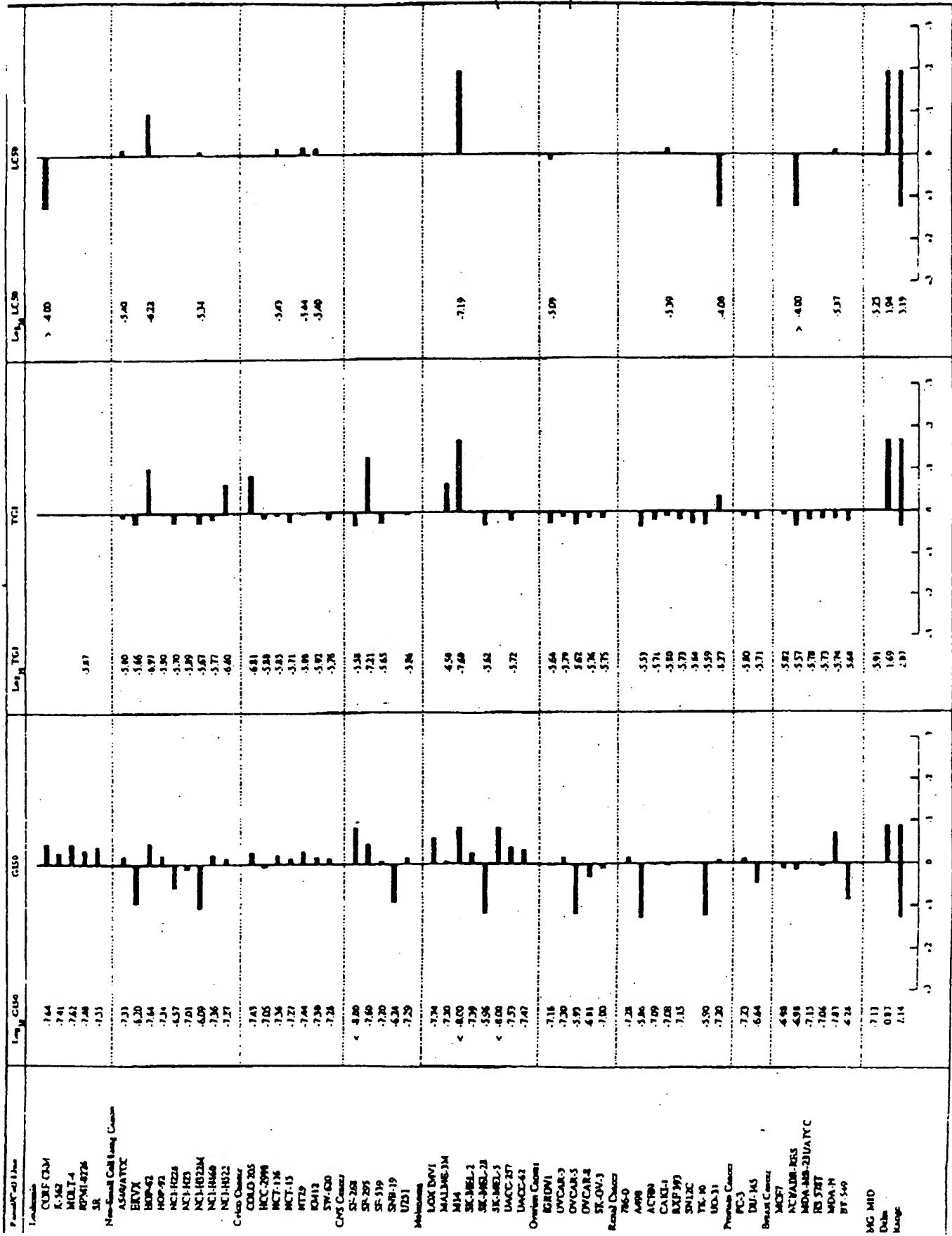


Figure 56

National Cancer Institute Developmental Therapeutics Program

Mean Graphs

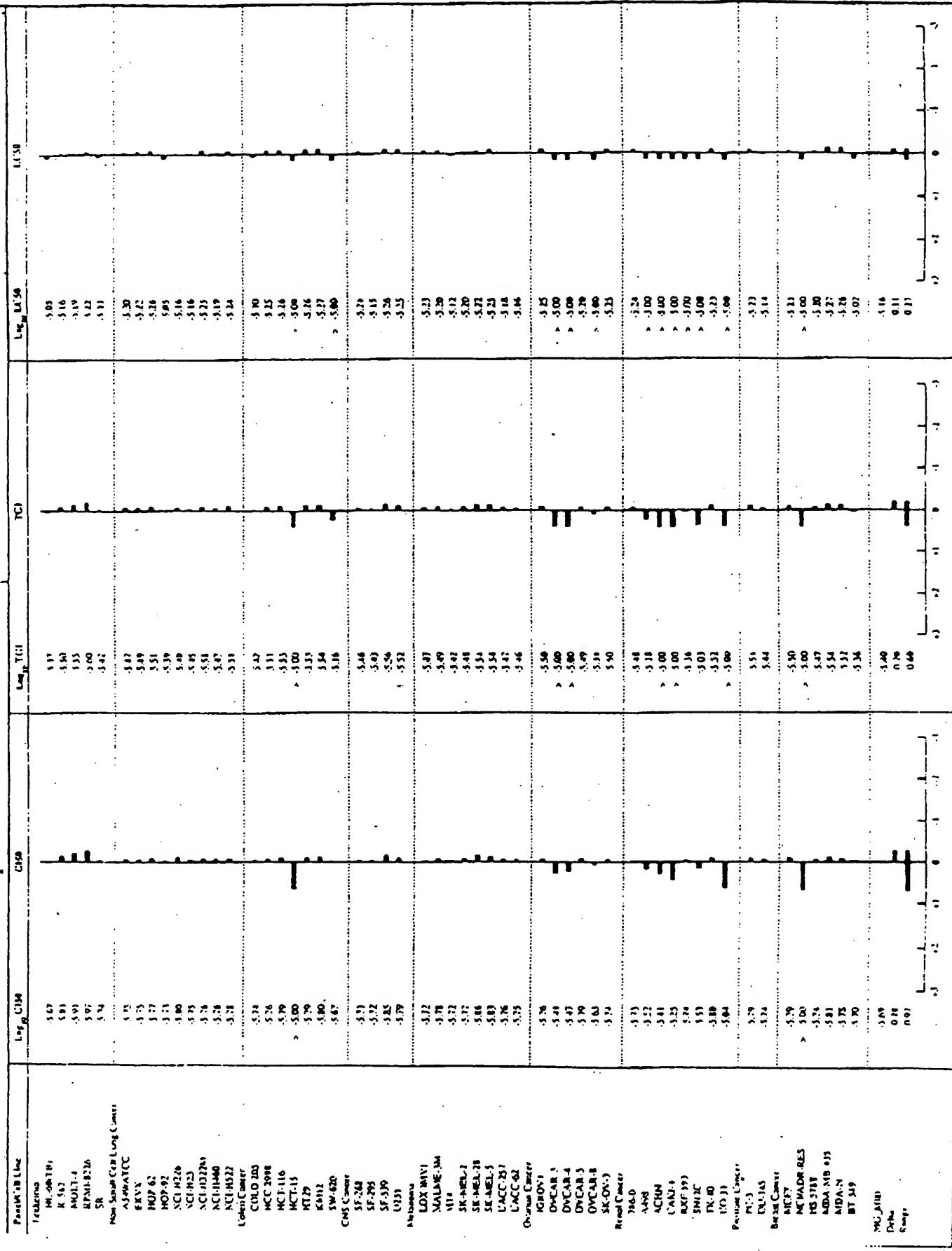


Figure 57

Mean (\bar{r}) graphs

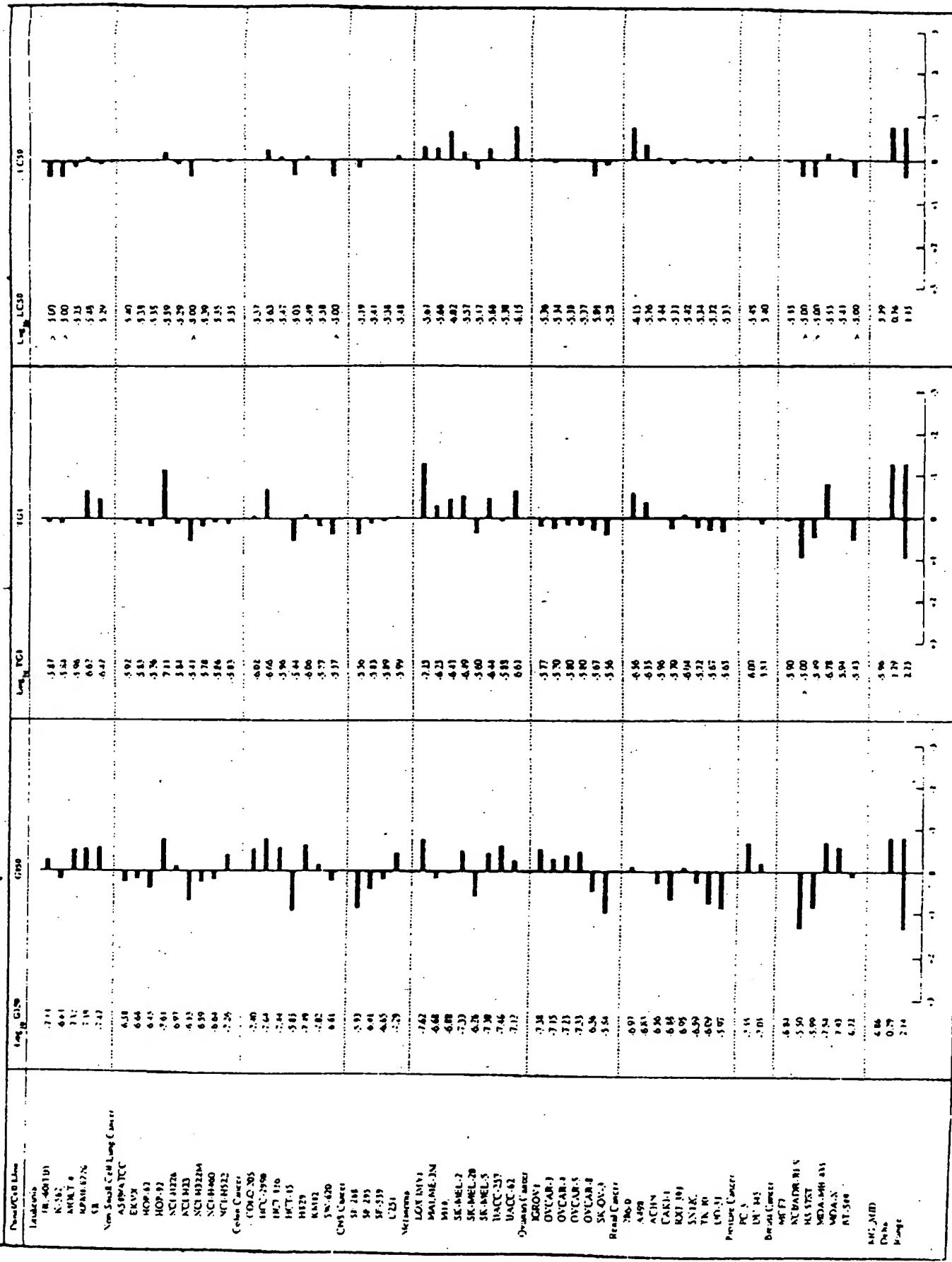


Figure 58

National Water Quality Monitoring and Diagnostic Program

Mean Graphs

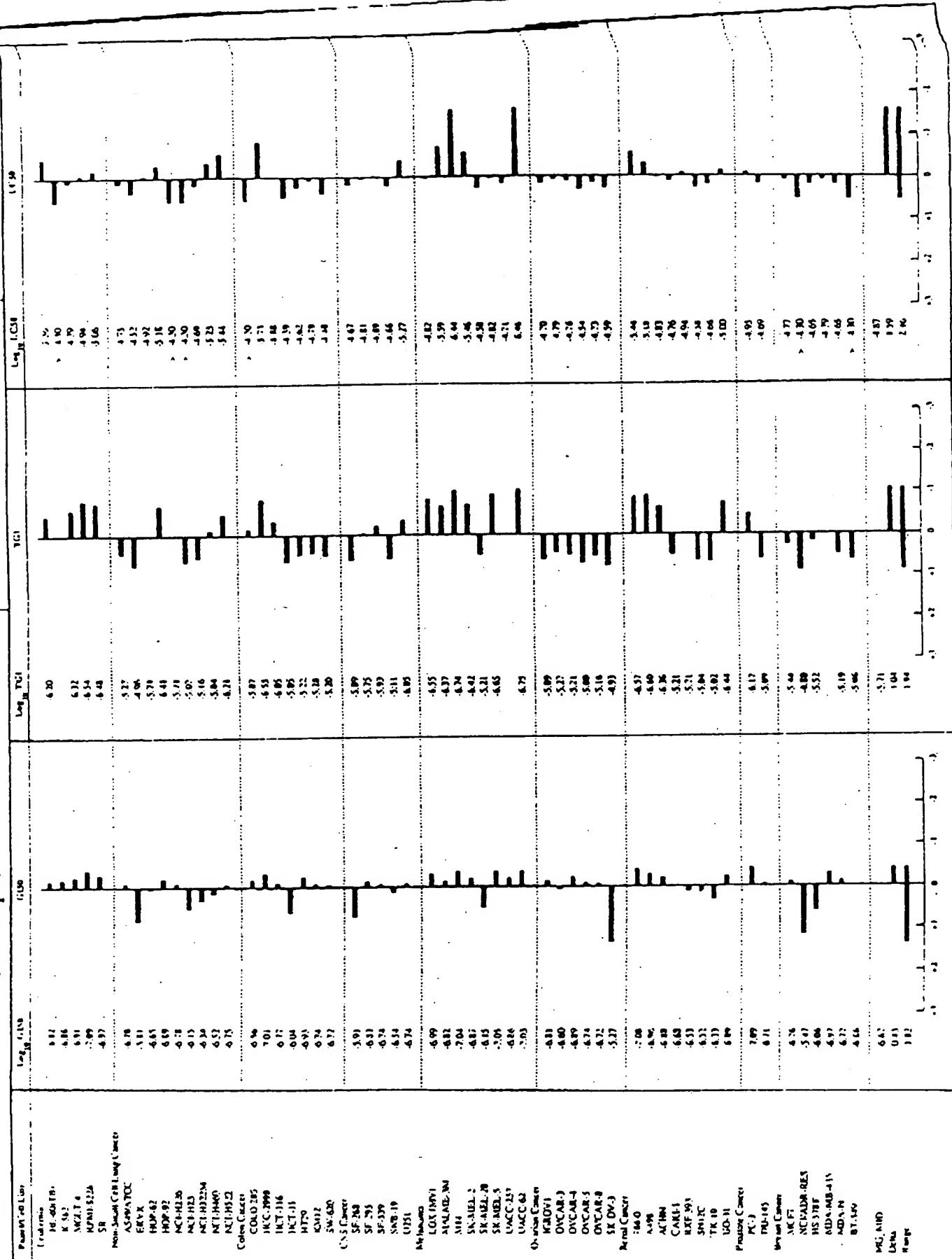


Figure 59

National Cancer Institute Developmental Therapeutics Program

Mean Graphs

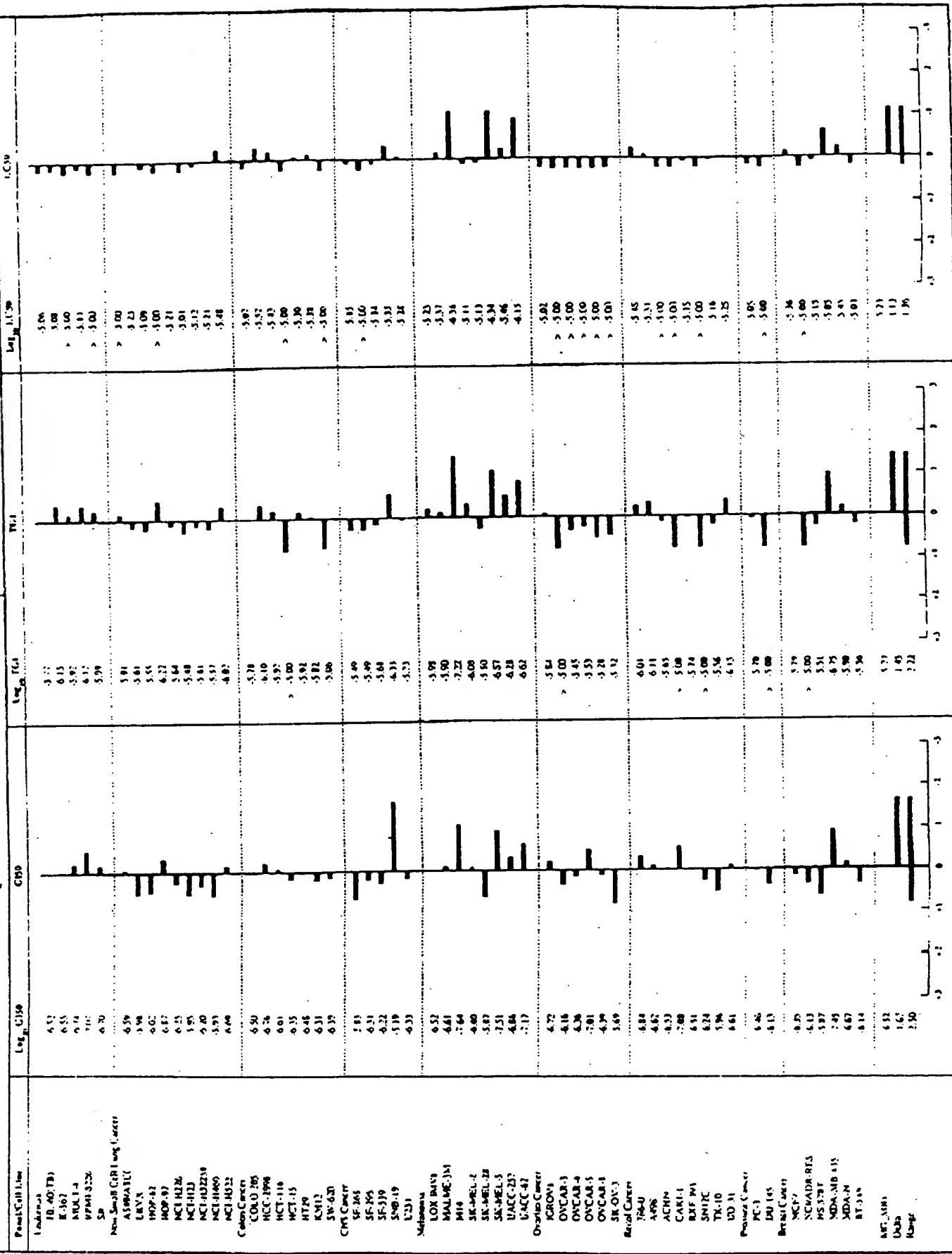


Figure 60

Mean (graphs)

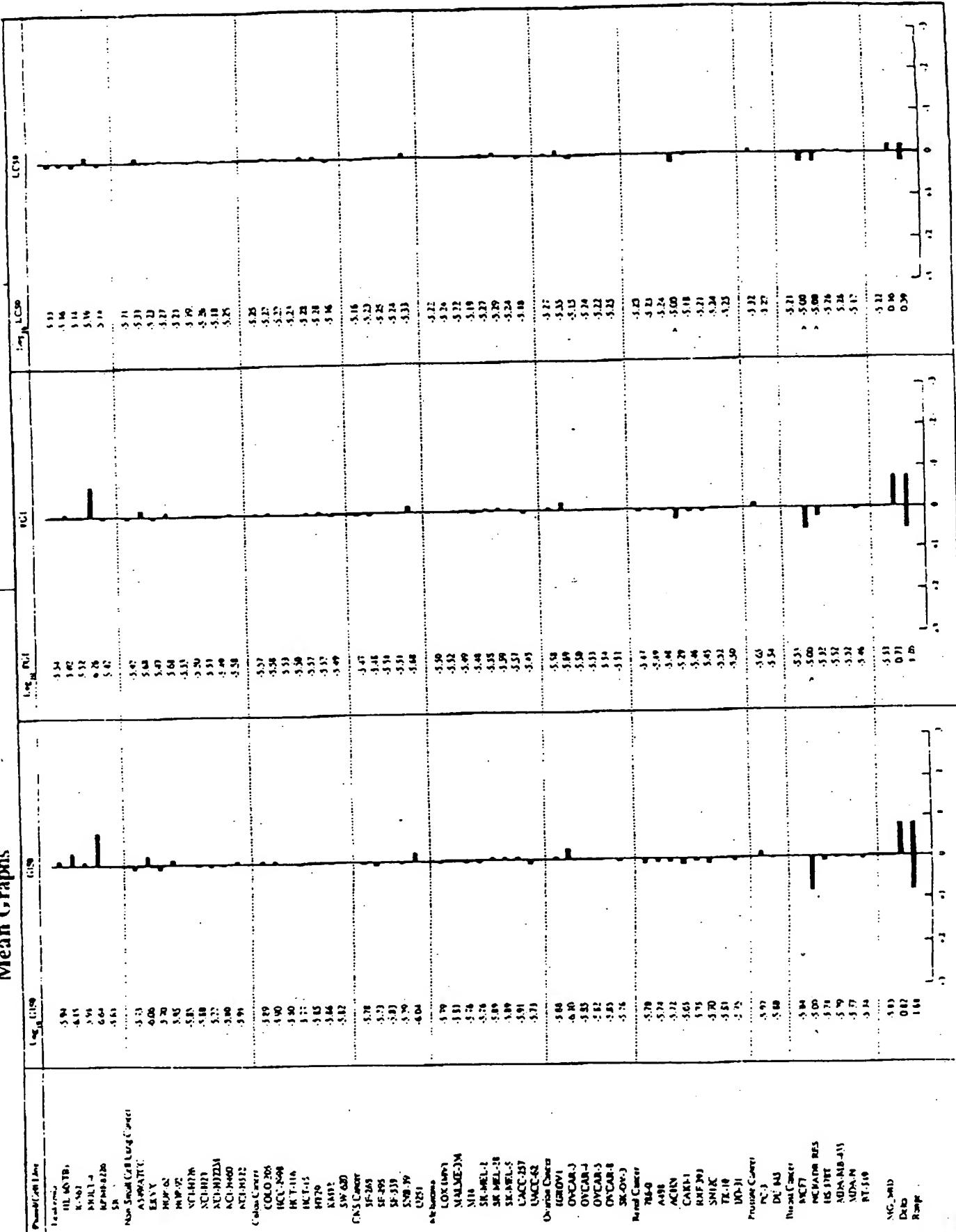


Figure 61

Mean Graphs

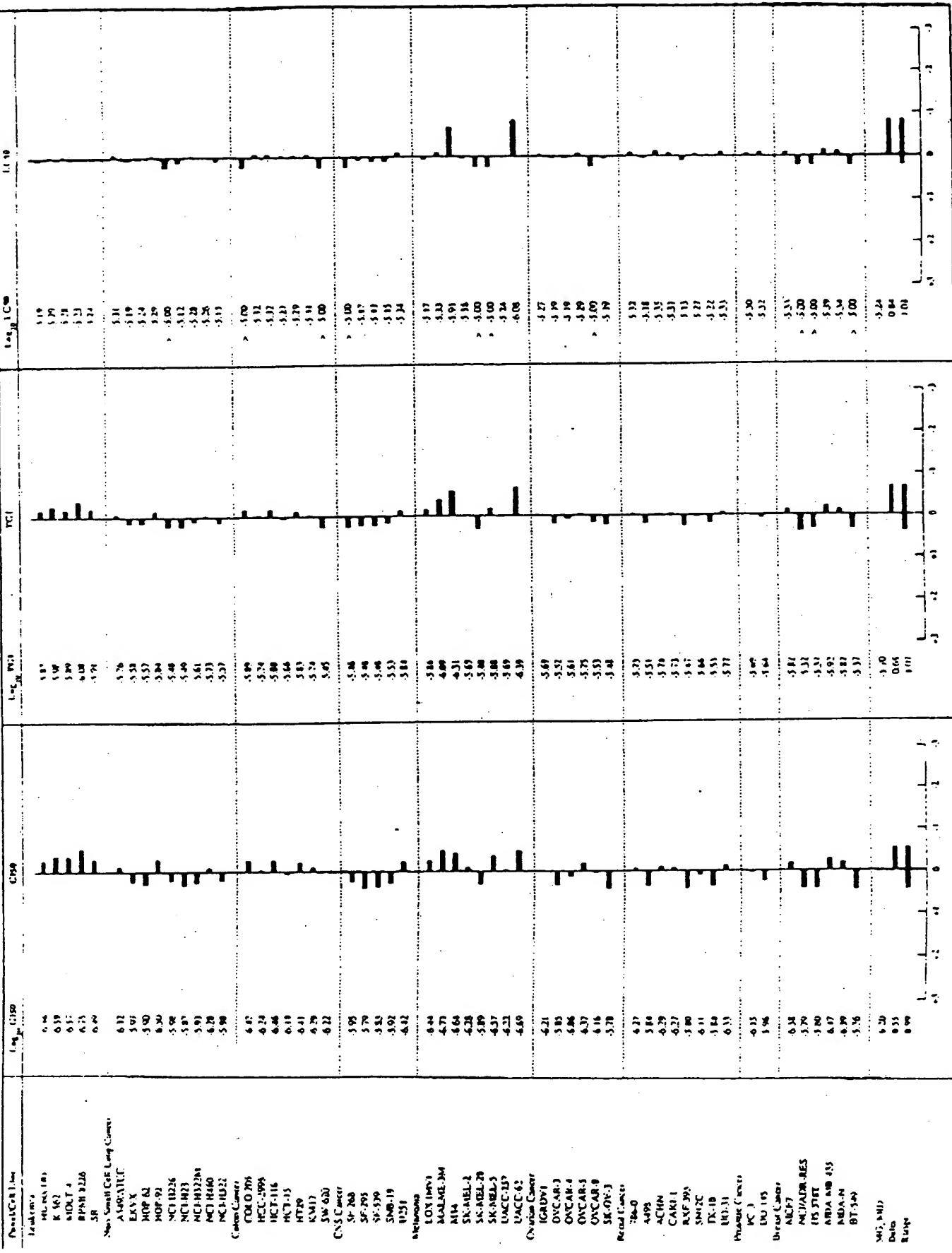


Figure 62